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The coauthors congratulate Academician I.L. Eremenko on his 70th jubilee

Cd(II) and Cd(II)–Eu(III) Complexes with Pentafluorobenzoic Acid Anions and N-Donor Ligands: Synthesis and Structures

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Abstract—The reactions of cadmium(II) and europium(III) pentafluorobenzoates ($([Cd(Pfbz)(H_2O)_4^+\}_n \cdot n(Pfbz)^-]$ (**I**) and $[Eu_2(Pfbz)_6(H_2O)_8] \cdot 2H_2O$ (**II**), respectively; Pfbz is pentafluorobenzoic acid anion) with the N-donor ligands (pyridine (Py), 2-phenylpyridine (Phpy), and 3-ethynylpyridine (Etypy)) afford a series of new Cd–Ln complexes with $Pfbz^-$ anions and Py or its substituted analogues: $[Cd_2Eu_2(Pfbz)_{10}(Py)_4]$ (**III**), $[Cd_2Eu_2(Pfbz)_{10}(Phpy)_2(MeCN)_2] \cdot 5MeCN$ (**IV**), and $[CdEu_2(Pfbz)_8(Etypy)(H_2O)_2]_n \cdot 3n MeCN \cdot n(Etypy)$ (**VI**). Similar reactions of compounds **I** and **II** with 2,4-lutidine (Lut), isoquinoline (Iquin), 2,2'-biquinoline (Biquin), and 7,8-benzoquinoline (Bquin) give the following cadmium complexes as the major products of crystallization from the reaction solutions: $[Cd(Pfbz)_2(Lut)]_n$ (**V**), $[Cd(H_2O)(Pfbz)_2(Iquin)_2]_n$ (**VII**), $[Cd(Pfbz)_2(Biquin)]$ (**VIII**), and $[Cd(Pfbz)_3]_n^- \cdot n(HBquin)^+$ (**IX**), respectively. The X-ray diffraction data (CIF files CCDC nos. 1987805 (**I**), 1987808 (**III**), 1987829 (**IV**), 1987817 (**V**), 1987822 (**VI**), 1987823 (**VII**), 1987824 (**VIII**), and 1987826 (**IX**)) are examples of the formation of new unusual coordination polymers.

Keywords: cadmium, europium, pentafluorobenzoic acid, coordination polymers, X-ray diffraction analysis

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INTRODUCTION

One of the main distinctions of cadmium from 3*d* metals in the carboxylate systems is the pronounced affinity to form coordination polymers (metal-organic frameworks (MOF)) due to the elongation of Cd–X bonds (X is any atom of the coordination environment of cadmium) compared to 3*d* metals. For example, Ni(II), Co(II), and Zn(II) acetates crystallize from aqueous solutions as mononuclear complexes $[M(OAc)_2(H_2O)_4]$ (Zn [1], Co [2], and Ni [3]), and cadmium acetate crystallizes in the form of 1D MOF $[Cd(OAc)_2(H_2O)_2]_n$ [4]. Cadmium diaquadicarboxylates with more bulky substituents have molecular structures [5–7], since an increase in the hydrocarbon substituent sizes results in steric hindrances preventing bringing together the mononuclear fragments at the distances at which polynuclear fragments are formed. The structures of the 3*d*-metal compounds $[M(O_2CR)_2L]$, where L is pyridine or its monodentate derivative, are binuclear, as a rule (Co [8, 9], Zn [10, 11], and Ni [12, 13]), whereas the acetate [14] and 3,5-dibromobenzoate [15] MOF with the analogous composition of the monomeric fragment are known for cadmium.

Probably, the formation of the carboxylate MOF can also be observed for other anions of monocarboxylic acids if no steric hindrances appear that favor the formation of molecular rather than polymeric structures. A favorable factor for polymerization is the presence of any nonvalent interactions facilitating bringing together and the achievement of the mutual orientation of individual structural fragments. This can be caused by hydrogen bonds or aromatic stacking fragments.

The considered examples demonstrate that the “geometry” of ligands is very important for overcoming steric hindrances and forming polymeric structures. In particular, the presence of small substituents or their planar structure, as in the case of aromatic fragments, is significant.

One should give attention to the known systems of organic compounds in which perfluorinated and nonfluorinated aromatic fragments are combined [16–18]. These systems are typical of the parallel arrangement of all aromatic cycles and their bringing together at the distances to ~3.4–3.6 Å. This is well illustrated by the crystal packing of benzene and hexafluorobenzene with the same “ladder” motif of the crystal packing, whereas their cocrystallizate $C_6H_6 \cdot C_6F_6$ has a layered dense packing [19]. The effect was studied in detail for the organic fluorine-substituted and unsubstituted molecules [20].

Compound $[Cd(Pfbz)_2(Bipy)(H_2O)]_n$ (Bipy is 2,2'-bipyridine) has recently been the single known cadmium pentafluorobenzoate polymer [21]. The authors attribute the stabilization of the polymeric structure of this complex to the presence of hydrogen bonds, C–H...F–C contacts, and stacking interactions in it. It is important that in this compound the cadmium complex simultaneously coordinate the ligands containing unsubstituted and perfluorinated aromatic substituents. The fact of MOF formation with the chelating Bipy ligand indicates, most likely, in favor of the fact that a tendency to form MOF containing various monodentate and, possibly, chelating pyridine derivatives will probably be observed for the pentafluorobenzoate systems as in the case of the acetate systems.

Our studies are not restricted by the cadmium complexes and are aimed, to a higher extent, at synthesizing Cd–Ln heterometallic MOF. The latter attract attention due to the nontrivial photoluminescence properties of lanthanide ions, in particular, europium(III), whose emission lies in the red range of the visible spectrum [22]. These compounds can be used as optical amplifiers and sensor materials for luminescent films, and the formation of intramolecular π–π interactions can exert a positive effect on the luminescence quantum yields [23]. Nowadays the Cd(II) heterometallic compounds are much more poorly studied. They are interesting from the point of view that their coordination polymers will be built of tri- or tetranuclear heterometallic fragments typical of molecular heterometallic systems [23].

The purpose of this work is the synthesis of the pentafluorobenzoate complexes of cadmium and pyridine or its derivatives as the aromatic N-donor ligand to test the possibility of binding the fragments of the complex between each other in the crystalline lattice to form polymeric structures.

EXPERIMENTAL

All procedures related to the synthesis of new complexes were carried out in air using acetonitrile (≥99.5%) and distilled water. The following reagents were used: $Cd(NO_3)_2 \cdot 4H_2O$ (99+%, Acros organics), $Eu(NO_3)_3 \cdot 6H_2O$ (99.99%, Lanhit), KOH (reagent grade, Reakhim), pentafluorobenzoic acid (HPfbz, 99%, P&MInvest), pyridine (Py, ROTIPURAN® ≥ 99.5%), 2-phenylpyridine (Phpy, Sigma-Aldrich, 98%), 2,4-lutidine (Lut, Sigma-Aldrich, 99%), 3-ethynylpyridine (Etypy, Sigma-Aldrich, 98%), isoquinoline (Iquin, Sigma-Aldrich, 98%), 2,2'-biquinoline (Biquin, Sigma-Aldrich, 98%), and 7,8-benzoquinoline (Bquin, Sigma-Aldrich, 97%). The IR spectra of the compounds were recorded on a Spectrum 65 FTIR spectrophotometer (PerkinElmer) using the attenuated total internal reflection mode (ATR) in the frequency range 400–4000 cm^{-1}. Elemental analyses were conducted on a EuroEA 3000 CHNS analyzer (EuroVector).

Synthesis of $[\{Cd(Pfbz)(H_2O)_4^+\}_n \cdot n(Pfbz)^-]$ (I). Compound HPfbz (1.368 g, 6.484 mmol) was added to freshly precipitated $Cd(OH)_2$ (0.475 g, 3.242 mmol), which was prepared by the reaction of $Cd(NO_3)_2 \cdot 4H_2O$ (1.000 g, 3.242 mmol) and KOH (0.363 g, 6.484 mmol) in water (100 mL). The reaction mixture was stirred at 80°C for 4 h until a precipitate of $Cd(OH)_2$ was completely dissolved. The reaction solution was kept at room temperature with slow evaporation. Colorless crystals formed in 6 days and suitable for X-ray diffraction analysis (XRD) were decanted from the mother liquor and dried in air. The yield of complex **I** was 1.494 g (86.3% based on $Cd(NO_3)_2 \cdot 4H_2O$).

For $C_{14}H_8O_8F_{10}Cd$

Anal. calcd., %	C, 27.72	H, 1.33
Found, %	C, 27.88	H, 1.69

IR (ATR), ν, cm^{-1}: 3380 s, 1653 m, 1706 w, 1644 m, 1563 m, 1529 s, 1473 s, 1394 s, 1370 s, 1365 s, 1300 m, 1121 s, 985 s, 940 m, 925 m, 821 w, 810 w, 772 m, 744 m, 587 m, 506 m.

Synthesis of $[Eu_2(Pfbz)_6(H_2O)_8] \cdot 2H_2O$ (II). Compound HPfbz (2.052 g, 9.726 mmol) was added to freshly precipitated $Eu(OH)_3$ (0.603 g, 3.242 mmol), which was prepared by the reaction of $Eu(NO_3)_3 \cdot 6H_2O$ (1.446 g, 3.242 mmol) and KOH (0.545 g, 9.726 mmol) in water (100 mL). The mixture was stirred at 80°C for 6 h to the complete dissolution of a precipitate of $Eu(OH)_3$. The reaction solution was kept at room temperature with slow evaporation. Colorless crystals formed in 10 days and suitable for XRD were decanted from the mother liquor and dried in air. The yield of complex **II** was 1.737 g (61.2% based on $Eu(NO_3)_3 \cdot 6H_2O$).

For $C_{42}H_{20}O_{22}F_{30}Eu_2$

Anal. calcd., %	C, 28.82	H, 1.15
Found, %	C, 28.31	H, 1.55

IR (ATR), ν, cm^{-1}: 3633 w, 1650 m, 1590 s, 1522 m, 1488 w, 1498 s, 1430 s, 1401 s, 1380 s, 1294 m, 1115 s, 990 s, 945 m, 932 w, 826 w, 773 s, 745 s, 704 w, 654 w, 619 w, 583 w, 507 s, 496 w, 477 m.

Synthesis of [$Cd_2Eu_2(Pfbz)_{10}(Py)_4$] (III). A weighed sample of compound **II** (0.145 g, 0.083 mmol) was added to a solution of complex **I** (0.100 g, 0.166 mmol) in MeCN (5 mL). The reaction mixture was stirred at 70°C for 20 min, and pyridine (27 μL, 0.322 mmol, Cd : L = 1 : 2) was added to the hot solution. The obtained colorless solution was kept at 70°C in a closed vial. Colorless crystals formed in 3 days and suitable for XRD were decanted from the mother liquor and washed with cold acetonitrile (*T* ≈ 5°C). The yield of complex **III** was 0.187 g (38.1% based on compound **I**).

For $C_{90}H_{20}N_4O_{20}F_{50}Cd_2Eu_2$

Anal. calcd., %	C, 36.57	H, 0.68	N, 1.90
Found, %	C, 37.05	H, 0.43	N, 1.75

IR (ATR), ν, cm^{-1}: 1651 m, 1585 s, 1525 s, 1488 s, 1449 w, 1385 s, 1293 m, 1224 w, 1142 w, 1108 m, 1070 m, 1040 m, 991 s, 933 s, 829 m, 767 m, 743 s, 700 s, 681 m, 631 m, 609 w, 583 m, 507 m.

Synthesis of [$Cd_2Eu_2(Pfbz)_{10}(Phpy)_2(MeCN)_2$] · 5MeCN (IV) was carried out according to a procedure similar to that for compound **III** using Phpy (237 μL, 1.663 mmol, Cd : L = 1 : 10) instead of Py. Colorless crystals formed in 10 days and suitable for XRD were decanted from the mother liquor and washed with cold acetonitrile (*T* ≈ 5°C). The yield of complex **IV** was 0.168 g (62.3% based on compound **I**).

For $C_{106}H_{39}N_9O_{20}F_{50}Cd_2Eu_2$

Anal. calcd., %	C, 39.77	H, 1.21	N, 3.87
Found, %	C, 39.29	H, 1.40	N, 3.61

IR (ATR), ν, cm^{-1}: 3451 w, 2630 w, 2253 w, 1650 m, 1627 m, 1598 s, 1574 m, 1521 m, 1493 s, 1454 m, 1426 m, 1402 s, 1297 m, 1158 m, 1118 m, 1108 s, 994 s, 942 s, 935 m, 895 w, 831 m, 771 m, 747 s, 695 s, 639 m, 626 w, 582 s, 549 w, 507 m, 481 m.

Synthesis of [$Cd(Pfbz)_2(Lut)$]$_n$ (V) was carried out according to a procedure similar to that for compound **III** using Lut (193 μL, 1.663 mmol, Cd : L = 1 : 10) instead of Py. Colorless crystals formed in 2 days and suitable for XRD were decanted from the mother liquor and washed with cold acetonitrile (*T* ≈ 5°C). The yield of complex **V** was 0.109 g (51.1% based on compound **I**).

For $C_{21}H_9NO_4F_{10}Cd$

Anal. calcd., %	C, 39.31	H, 1.41	N, 2.18
Found, %	C, 39.12	H, 1.39	N, 2.02

IR (ATR), ν, cm^{-1}: 1647 m, 1601 s, 1520 m, 1489 s, 1441 m, 1371 s, 1305 m, 1291 w, 1180 w, 1140 w, 1114 m, 1100 m, 990 c, 928 c, 831 c, 822 m, 767m, 755 m, 742 s, 701 w, 692 w, 619 w, 582 w, 561 w, 541 m, 506 m, 481 w.

Synthesis of [$CdEu_2(Pfbz)_8(Etypy)(H_2O)_2$]$_n$ · 3*n*MeCN · *n*(Etypy) (VI) was carried out according to a procedure similar to that for compound **III** at room temperature using Etypy (0.173 g, 1.663 mmol, Cd : L = 1 : 10) instead of Py. The resulting reaction mixture was kept at 3°C for 30 days. The formed colorless crystals suitable for XRD were decanted from the mother liquor and washed with cold acetonitrile (*T* ≈ 5°C). The yield of complex **VI** was 0.132 g (32.4% based on compound **I**).

For $C_{76}H_{23}N_5O_{18}F_{40}CdEu_2$

Anal. calcd., %	C, 36.97	H, 0.89	N, 2.84
Found, %	C, 36.83	H, 1.01	N, 2.77

IR (ATR), ν, cm^{-1}: 2819 w, 2546 w, 2294 w, 2252 m, 1652 m, 1610 s, 1523 m, 1494 s, 1392 s, 1293 m, 1192 w, 1108 s, 994 s, 931 m, 826 m, 769 m, 742 s, 699 m, 674 w, 647 w, 583 w, 508 m, 487 m, 477 m, 458 m, 418 w.

Synthesis of [$Cd(H_2O)(Pfbz)_2(Iquin)_2$]$_n$ (VII) was carried out according to a procedure similar to that for compound **III** using Iquin (196 μL, 1.663 mmol, Cd : L = 1 : 10) instead of Py. Colorless crystals formed in 2 days and suitable for XRD were decanted from the mother liquor and washed with cold acetonitrile (*T* ≈ 5°C). The yield of complex **VII** was 0.106 g (79.1% based on compound **I**).

For $C_{32}H_{16}N_2O_5F_{10}Cd$

Anal. calcd., %	C, 47.44	H, 1.99	N, 3.45
Found, %	C, 47.92	H, 2.13	N, 3.33

IR (ATR), ν, cm^{-1}: 3005 w, 2293 w, 2253 m, 1654 m, 1513 m, 1492 s, 1443 m, 1374 s, 1319 m, 1285 m, 1109 s, 1038 w, 992 s, 955 m, 918 m, 812 m, 783 m, 743 m, 635 m, 516 m, 489 m, 466 m.

Synthesis of [$Cd(Pfbz)_2(Biquin)$] (VIII) was carried out according to a procedure similar to that for compound **III** using Biquin (0.043 mg, 0.166 mmol, Cd : L = 1 : 1) instead of Py. Colorless crystals formed in 5 days and suitable for XRD were decanted from the mother liquor and washed with cold acetonitrile (*T* ≈ 5°C). The yield of complex **VIII** was 0.106 g (79.1% based on compound **I**).

For $C_{32}H_{12}N_2O_4F_{10}Cd$

Anal. calcd., %	C, 48.60	H, 1.53	N, 3.54
Found, %	C, 48.11	H, 1.74	N, 3.69

IR (ATR), ν, cm^{-1}: 2919 w, 1653 m, 1584 c, 1520 m, 1490 c, 1421m, 1400 m, 1379 c, 1340 m, 1296 m, 1186 w, 1142 w, 1103 c, 992 c, 950m, 936 m, 824 m, 767 m, 747 m, 694 m, 656 w, 619 w, 584 w, 507 m, 488 m, 479 w.

Table 1. Crystallographic parameters and structure refinement details for compounds **I** and **III–V**

Parameter	Value			
	I	**III**	**IV**	**V**
Empirical formula	$C_{14}H_8O_8F_{10}Cd$	$C_{90}H_{20}N_4O_{20}F_{50}Cd_2Eu_2$	$C_{106}H_{39}N_9O_{20}F_{50}Cd_2Eu_2$	$C_{21}H_9NO_4F_{10}Cd$
FW	606.61	2955.82	3237.18	641.69
T, K	296(2)	173(2)	120(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$C2/C$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	37.928(18)	13.368(4)	14.2202(6)	6.664(5)
b, Å	7.455(3)	24.908(7)	14.6418(6)	12.817(9)
c, Å	13.217(8)	15.352(5)	15.7217(7)	13.736(15)
α, deg	90	90	78.294(1)	112.99(3)
β, deg	108.07(4)	109.396(5)	70.134(1)	97.46(4)
γ, deg	90	90	67.406(1)	90.55(2)
V, Å^3	3553(3)	4822(3)	2832.4(2)	1068.5(16)
Z	8	2	1	2
ρ_{calc}, g cm^3	2.239	2.036	1.898	1.995
μ, mm^{-1}	1.377	1.888	1.617	1.140
θ_{max}, deg	25.43	24.999	30.61	25.669
T_{min}/T_{max}	0.601/0.745	0.634/0.785	0.817/0.855	0.620/0.745
Number of measured reflections	12422	24257	27883	8758
Number of independent reflections	3300	7986	11137	3998
Number of reflections with $I > 2\sigma(I)$	2703	7980	9928	3255
R_{int}	0.0772	0.1600	0.019	0.0466
Number of refined parameters	2308	4017	9018	2934
GOOF	1.010	0.967	1.036	1.109
R_1 ($I > 2\sigma(I)$)	0.0433	0.0767	0.0289	0.0639
wR_2 ($I > 2\sigma(I)$)	0.0901	0.2037	0.0690	0.1298
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	–4.660/2.451	–1.232/1.509	–1.371/1.537	–1.156/1.007

Synthesis of $[Cd_2(Pfbz)_3]_n^- \cdot n$HBquin$^+$ (IX) was carried out according to a procedure similar to that for compound **III** using Bquin (0.297 g, 1.663 mmol, Cd : L = 1 : 10) instead of Py. Colorless crystals formed in 8 days and suitable for XRD were decanted from the mother liquor and washed with cold acetonitrile ($T \approx$ 5°C). The yield of complex **IX** was 0.055 g (35.9% based on compound **I**).

For $C_{68}H_{20}N_2O_{12}F_{30}Cd_2$

Anal. calcd., %	C, 47.44	H, 1.99	N, 3.45
Found, %	C, 47.92	H, 2.13	N, 3.33

IR (ATR), ν, cm^{-1}: 3070 w, 2628 w, 2243 w, 1661 m, 1643 m, 1591 s, 1566 m, 1523 m, 1490 s, 1480 s, 1443 m, 1391 s, 1371 s, 1291 s, 1277 s, 1269 m, 1208 s, 1146 w, 1112 s, 1104 s, 990 s, 928 s, 876 m, 832 m, 823 m, 771 m, 742 m, 706 m, 697 m, 684 m, 652 m, 616 w, 583 m, 533 m, 505 m, 477 m.

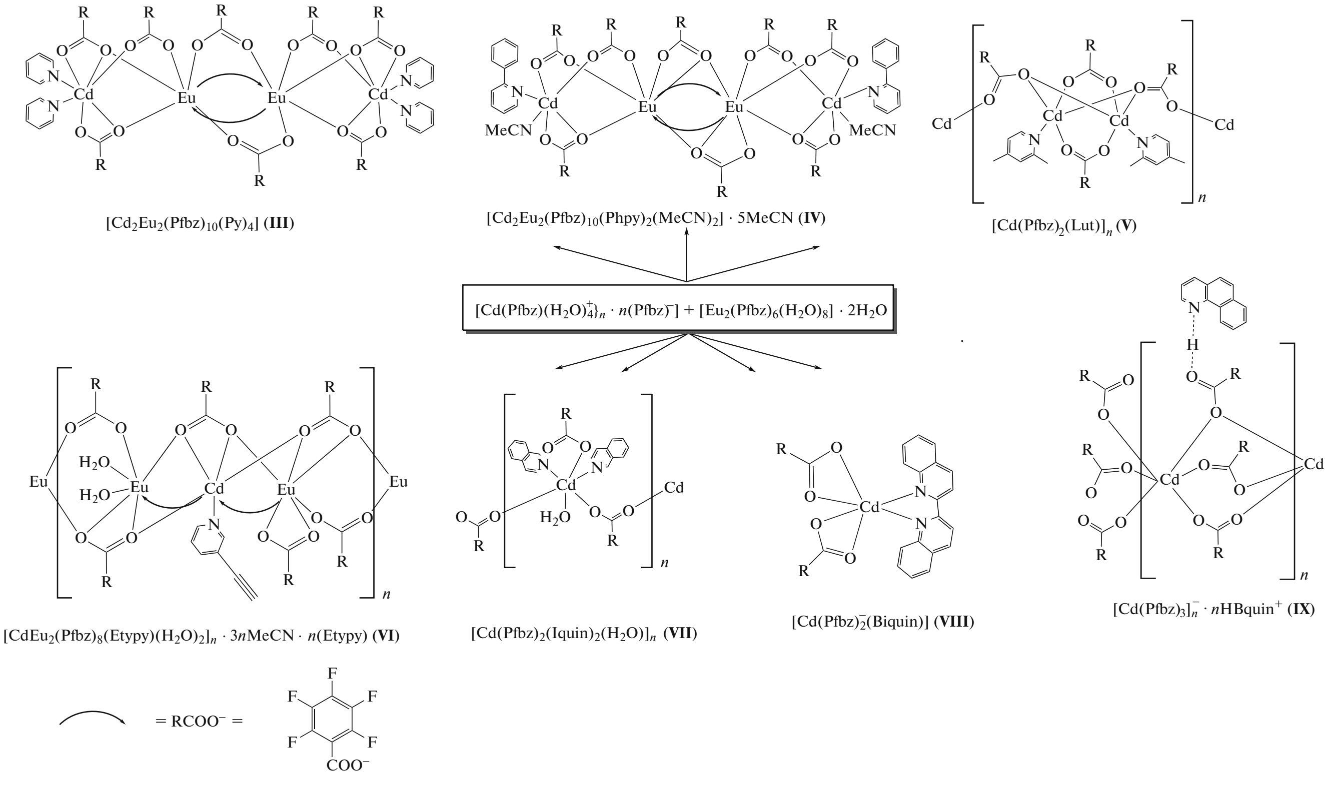
XRD analyses of the single crystals of compounds **I–VI** and **VIII–IX** were conducted on a Bruker Apex II diffractometer equipped with a CCD detector (MoK_α, λ = 0.71073 Å, graphite monochromator) [24]. A semiempirical absorption correction was applied for all compounds using the SADABS program [25]. 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 geometrically generated and refined by the riding model. The calculations were performed by the SHELX program package [26] using OLEX2 [27].

The XRD data for complex **VII** were obtained on the X-ray beam of the Belok station of the Kurchatov Synchrotron Radiation Source at the Kurchatov Institute Russian Research Center (Moscow, Russia) in the φ scan mode using a Rayonix SX165 CCD detector at 100 K ($\lambda = 0.79312$ Å). The primary indexing was performed, the parameters were refined, the reflections were integrated, and an absorption correction was applied using the XDS program package [28]. The structure was solved by a direct method 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 by the riding model. The calculations were performed using the SHELXTL program package [26]. The geometry of polyhedra of metal atoms was determined using the SHAPE 2.1 program [29, 30]. The crystallographic parameters and structure refinement details for compounds **I** and **III**–**IX** are presented in Tables 1 and 2. Selected bond lengths and bond angles for complex **I** are given in Table 3.

The full sets of the XRD parameters for compounds **I** and **III**–**IX** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1987805 (**I**), 1987808 (**III**), 1987829 (**IV**), 1987817 (**V**), 1987822 (**VI**), 1987823 (**VII**), 1987824 (**VIII**), and 1987826 (**IX**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Compounds $[\mathrm{Cd(Pfbz)(H_2O)_4}]_n^+ \cdot n(\mathrm{Pfbz})^-]$ (**I**) and $[\mathrm{Eu_2(Pfbz)_6(H_2O)_8}] \cdot 2\mathrm{H_2O}$ (**II**) were synthesized by the reactions of cadmium(II) or europium(III) hydroxides with pentafluorobenzoic acid (HPfbz) in water typical of the syntheses of complexes with pentafluorobenzoic acid anions. The reactions of compounds **I** and **II** with the N-donor ligand (Py, Phpy, Lut, Etypy, Iquin, Biquin, Bquin) in a MeCN solution afforded a series of homo- and heterometallic complexes **III**–**IX**, respectively (Scheme 1). The reaction products were isolated as single crystals and characterized by CHN analysis, IR spectroscopy, and XRD. Based on the data obtained, we observed the formation of heterometallic complexes **III**–**VI** and cadmium complexes **VII**–**IX**.



Scheme 1.

Table 2. Crystallographic parameters and structure refinement parameters for compounds **VI**–**IX**

Parameter	Value			
	VI	**VII**	**VIII**	**IX**
Empirical formula	$C_{76}H_{23}N_5O_{18}F_{40}CdEu_2$	$C_{32}H_{16}N_2O_5F_{10}Cd$	$C_{32}H_{12}N_2O_4F_{10}Cd$	$C_{68}H_{20}N_2O_{12}F_{30}Cd_2$
FW	2470.31	810.89	790.75	1851.66
T, K	100(2)	150(2)	296(2)	296(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/C$	$P2_1/c$
a, Å	15.6773(11)	20.712(4)	14.5624(7)	15.6961(11)
b, Å	16.2440(17)	5.3510(11)	24.8057(12)	7.7640(6)
c, Å	18.5297(18)	26.889(5)	8.2876(4)	26.2157(19)
α, deg	83.888(4)	90	90	90
β, deg	71.098(3)	96.56(3)	106.471(2)	97.009(2)
γ, deg	65.635(3)	90	90	90
V, Å^3	4064.7(7)	2960.6(10)	2870.9(2)	3170.9(4)
Z	2	4	4	2
ρ_{calc}, g cm^3	2.018	1.819	1.830	1.939
μ, mm^{-1}	1.949	1.140	0.869	0.828
θ_{max}, deg	26.379	30.954	30.48	22.47
T_{min}/T_{max}	0.633/0.745	0.821/0.956	0.728/0.846	0.726/0.963
Number of measured reflections	28212	28266	27301	45636
Number of independent reflections	16077	21215	9914	9919
Number of reflections with $I > 2\sigma(I)$	8211	6715	4404	5659
R_{int}	0.0963	0.0439	0.0597	0.0975
Number of refined parameters	4716	5816	3956	4521
GOOF	0.964	1.054	1.065	1.083
R_1 ($I > 2\sigma(I)$)	0.0903	0.0503	0.0445	0.0533
wR_2 ($I > 2\sigma(I)$)	0.2260	0.1120	0.1098	0.1266
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	−3.127/2.649	−1.468/0.737	−0.758/ 0.700	−0.599/1.861

Complex **I** crystallizes in the monoclinic crystal system (space group *C*2/*c*). The metal atoms in the polymeric chain are translated by the 2_1 axis. Each Cd atom is bound to the adjacent pairs of the μ_2-bridging water molecules (O(1*w*) and O(2*w*), Fig. 1a). The metal atom builds up its nearest environment (CdO_8) to a square antiprism by the coordination of the Pfbz anion bound via the chelate mode and six water molecules, two of which are monodentate (O(3*w*) and O(4*w*)). The positive charge of the metal atom is compensated due to the outer-sphere Pfbz anion forming hydrogen bonds with the coordinated water molecules. The water molecule (O(4*w*)) forms hydrogen bonds with the O atoms of the coordinated Pfbz anions inside one chain. The O(2*w*) and O(3*w*) molecules form the hydrogen bond between the adjacent polymeric chains (Fig. 1b). Selected bond lengths and angles between the atoms involved in the hydrogen bonds of complex **I** are presented in Table 4.

A similar 1D complex is formed during the synthesis of cadmium tetrafluoroterephthalate in water [31], where the polymeric chain is formed by the bridging water molecules and the positive charge of the polymeric chain is compensated due to the second deprotonated $RCOO^-$ group, which is not involved in coordination, of the coordinated tetrafluoroterephthalate anion. In the case of 4-hydroxybenzoic acid anions (4-OHbnz), the mononuclear complex [Cd(4-

Table 3. Selected geometric characteristics of complexes **I**, **V**, and **VII–IX**

Bond	*d*, Å				
	I	**V**	**VII**	**VIII**	**IX**
Cd–N(L)		2.295(6)	2.323(4), 2.371(4)	2.306(2)	
Cd–O(H_2O)	2.310(4)–2.720(5)		2.282(4)		
Cd–O(Pfbz)	2.369(4)–2.497(5)	2.232(5)–2.512(5)	2.314(4)–2.381(4)	2.334(5)–2.392(5)	2.243(3)–2.351(4)
Cd...Cd	3.903	3.376(1), 5.254	5.353		3.912
Angle	ω, deg				
CdCdCd	144.64	96.760	180.00	96.760	165.849

Table 4. Geometric parameters of hydrogen bonds in the crystal structure of compound **I***

D–H...A	Distance, Å			Angle D–H...A, deg
	D–H	H...A	D...A	
O(1*w*)–H...O(4)^i	0.98	1.79	2.75	151.38
O(2*w*)–H...O(3)	0.96	1.66	2.72	174.65
O(3*w*)–H...O(3)	0.91	1.99	2.74	139.80
O(3*w*)–H...O(4)	0.92	1.97	2.77	144.38
O(4*w*)–H...O(1)^{ii}	0.85	1.98	2.81	164.45
O(4*w*)–H...O(2)^{iii}	0.93	1.98	2.57	122.92
O(2*w*)–H...O(3*w*)^{iii}	0.85	1.99	2.75	165.23

* Symmetry codes: ^{i} $x, 1 + y, z$; ^{ii} $-3/2 - x, -1/2 + y, 1/2 - z$; ^{iii} $-3/2 - x, 1/2 + y, 1/2 - z$.

OHBnz)$(H_2O)_5]^+(H_2O)$(4-OHBnz)$^-$ is formed [32] in which excess water molecules in the coordination sphere of the metal prevent the formation of the polymeric chain.

Complex **II** represents the known and structurally described compound [33, 34].

The reactions of compounds **I** and **II** in the presence of pyridine (Cd : L = 1 : 2) or 2-phenylpyridine (Cd : L = 1 : 10) result in the crystallization of linear tetranuclear complexes **III** and **IV** of similar structures (Figs. 2a and 2b, respectively). Complex **III** crystallizes in the monoclinic crystal system (space group $P2_1/c$), complex **IV** crystallizes in the tricnilic crystal system (space group $P\bar{1}$) as a solvate with MeCN molecules, and the inversion center in both compounds lies between the Eu(1) and Eu(1*A*) central atoms. The Eu atoms are linked to each other by two bridging and two chelate bridging Pfbz anions in complex **III** and by one chelate bridging and two bridging Pfbz anions in complex **IV**. In complex **III**, the Cd atom coordinates two Py molecules building up its environment (CdO_5N_2) to a pentagonal bipyramid. In complex **IV**, the environment of the Cd atom (CdO_4N_2) is built up to an octahedron by the coordination of the N atom of the Phpy and MeCN molecules. It is most likely that the presence of the bulky phenyl substituent in the Py molecule in the α position prevents the coordination of the second Phpy molecule, and the compact MeCN molecule exists in the coordination sphere of Cd. The geometry of the coordination environment of the Eu atom (EuO_8) in compounds **III** and **IV** corresponds to a square antiprism. The hydrogen atoms of Py, Phpy, and coordinated MeCN molecules participate in the formation of intermolecular C–H...F contacts with the atoms of the FPfbz anions (C...F 1.315–1.415 Å (in **III**), 1.336–1.348 Å (in **IV**), H...F 2.59–2.68 Å (in **III**) and 2.56–2.70 Å (in **IV**)); angles CHF lie in the ranges 111°–127° (for **III**) and 111°–138° (in **IV**)). Selected bond lengths and angles between the atoms involved in the hydrogen bonds of complexes **III** and **IV** are presented in Table 5.

Several examples of coordination compounds with monocarboxylic acid anions $\{Ln_2Cd_2\}$ in which 1,10-phenanthroline (Phen) acts as an N-donor ligand are known: $[Cd_2Ln_2(p\text{Tol})_{10}(\text{Phen})_2]$ (Ln = Nb, Pr, Sm) and $[Cd_2Ho_2(p\text{ClBnz})_{10}(\text{Phen})_2]$ (H(*p*Tol) is 4-methylbenzoic acid, H(*p*ClBnz) = 4-chlorobenzoic acid) [35]. In the complexes $[Zn_2Ln_2(O_2CR)_{10}(Py)_2]$ with monocarboxylic acid anions and pyridine, each zinc atom coordinates only one pyridine molecule (^-O_2CR is methacrylic acid anion, Ln(III) = Ce [36], ^-O_2CR is 1-naphthylacetic acid anion, Ln(III) = Eu, Dy, Tb [37]).

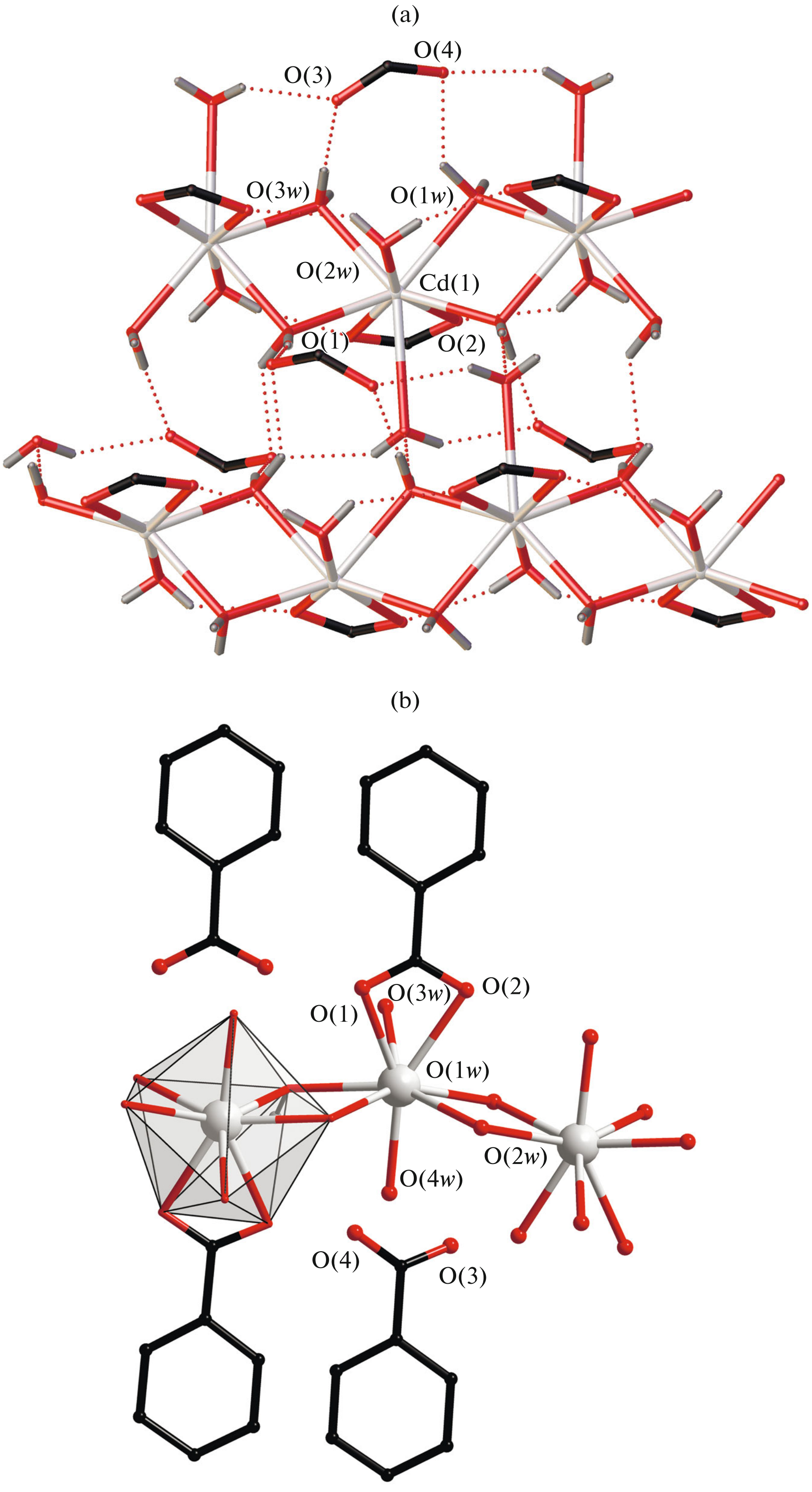


Fig. 1. Fragments of the (a) polymeric chain and (b) packing of complex **I** (fluorine atoms are omitted). Hydrogen and fluorine atoms (Fig. 1a) are omitted. The substituents at the carboxyl group (Fig. 1b) are omitted.

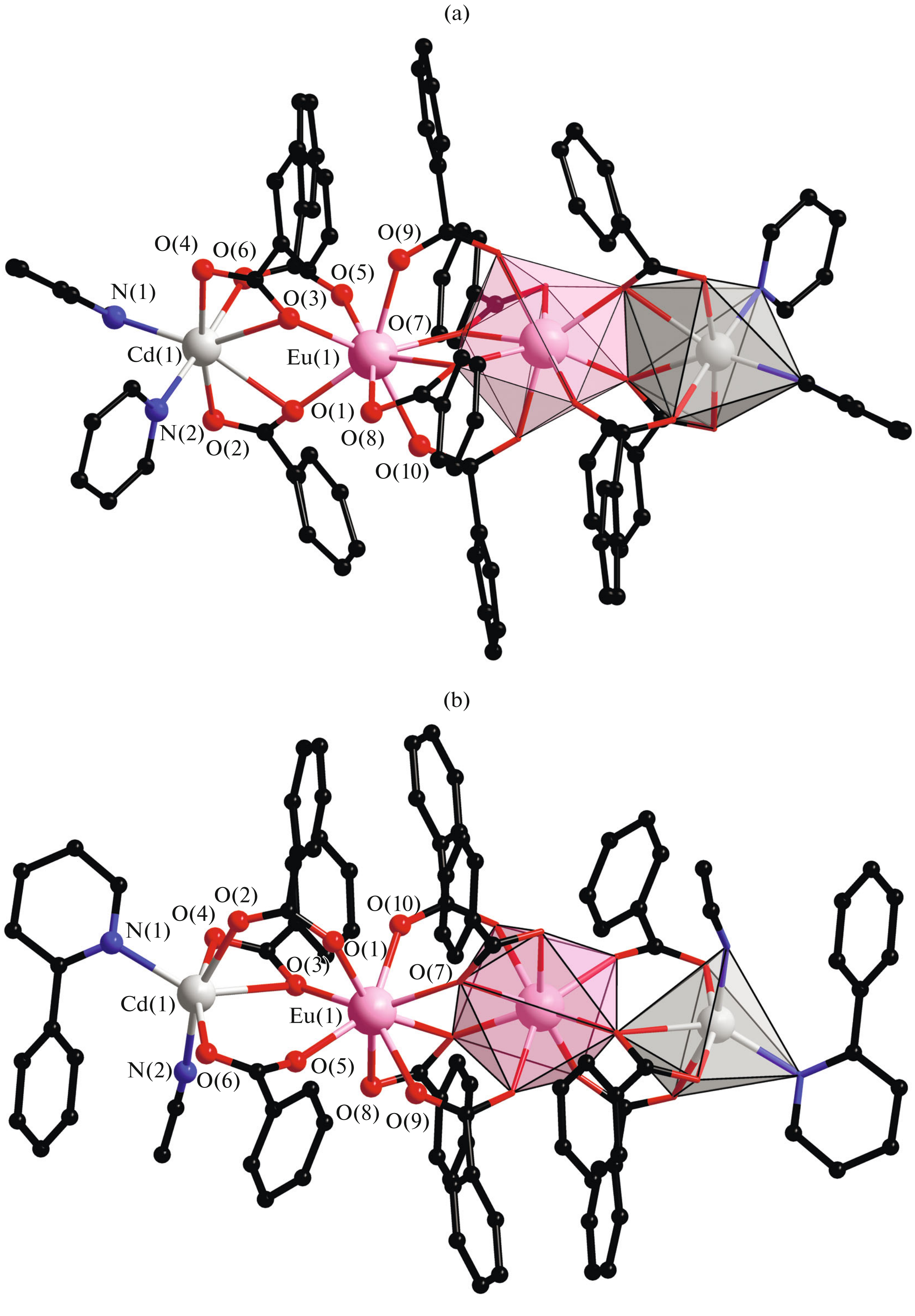


Fig. 2. Molecular structures of complexes (a) **III** and (b) **IV**. Hydrogen and fluorine atoms and solvates are omitted.

Two pyridine molecules coordinate to the zinc atom in the Ln–Zn complexes only in the case of the binuclear complex $[LnZn(Piv)_5(Py)_3]$ (Ln = Tb, Yb, Dy, Er; HPiv is trimethylacetic acid) [38]. No heterometallic complexes with 2-phenylpyridine molecules are described at the moment.

Complex **V** crystallizes in the triclinic crystal system with the space group $P\bar{1}$. The polymeric chain of

Table 5. Selected geometric characteristics of complexes **III**–**IV** and **VI**

Bond	*d*, Å		
	III	**IV**	**VI**
Cd–N(L)	2.271(11)–2.285(13)	2.290(3)	2.340(12)
M–X(Solv)		2.275(3) (MeCN)	2.414(9)–2.448(9) (H_2O)
Cd–O(Pfbz)	2.293(10)–2.540(9)	2.253(2)–2.371(3)	2.225(8)–2.724(9)
Eu–O(Pfbz)	2.337(10)–2.525(10)	2.305(2)–2.531(2)	2.322(9)–2.870(8)
Cd...Cd	11.683	12.030	10.202, 10.446
Cd...Eu	3.892	4.079	3.923, 4.087
Eu...Eu	3.920	3.926	4.216(2), 4.254(2)
Angle	ω, deg		
MMM	172.80 (CdEuEu)	168.411 (CdEuEu)	110.85, 111.45 (EuCdEu)

M = Eu or Cd, L is molecule of N-donor ligand. X = N or O of solvent molecule.

compound **V** is built of the centrosymmetric binuclear fragments $\{Cd_2(Pfbz)_4(Lut)_2\}$ (the inversion center is arranged between the Cd atoms) in which the metal atoms are linked by two μ_2-O,O'-bridging and two μ_2-O,O-bridging Pfbz anions (Fig. 3a). The latter Pfbz anions participate in the formation of the polymeric structure (Fig. 3b) coordinating via the monodentate coordination mode to the Cd atoms of two adjacent fragments $\{Cd_2(Pfbz)_4(Lut)_2\}$, and the bridging function of the carboxylate group corresponds to $\eta^1:\eta^2:\mu_3$. Thus, each cadmium atom coordinates five O atoms of five carboxylate groups and one N atom of the Lut molecule, and its environment (CdO_5N) corresponds to an octahedron.

The orientation of the aromatic fragments C_6F_5 and Lut inside one polymeric chain in the packing of complex **V** is close to parallel (the angle between the planes, the shortest distance between the planes, and the distance between the centroids are 5.2°, 3.287 Å, and 3.769 Å, respectively). This indicates the formation of stacking interactions between them. The formation of C–H...F contacts between the hydrogen atom of the CH_3 group of the Lut molecule and the F atom of the coordinated Pfbz anion of the adjacent polymeric chain (C–H...F 2.61, C...F 3.547 Å, angle C–H...F 166.4°) is also observed.

The cadmium compounds with 2,4-lutidine and monocarboxylic acid anions are presented in the literature only by several molecular complexes: $[Cd_2(Piv)_4(Lut)_2$ [39] and $[Cd_2M(Piv)_6(Lut)_2]$ (M = Ca, Sr, Mg) [40].

Complex **VI** crystallizes in the triclinic crystal system with the space group $P\overline{1}$ as a solvate with three MeCN molecules and one Etypy molecule. Complex **IV** is a 1D polymer in which the elementary unit is the trinuclear fragment $\{Eu_2Cd(Pfbz)_8(H_2O)_2(Etypy)\}$ (Fig. 4a). In this fragment, the Cd(1) atom is linked with each europium atom, Eu(1) and Eu(2), by one bridging and two chelate bridging Pfbz anions. The environment of the cadmium atom consists of two O atoms of two μ_2-O,O'-bridging Pfbz anions, two O atoms of two η^2,μ_3-chelate bridging Pfbz anions bound via the chelate mode to the Eu atom, two O atoms of the η^2,μ_3-chelate bridging Pfbz anion, which is coordinated via the chelate mode to the Cd atom, and one N atom of the Etypy molecule. The environments of the Eu(1) and Eu(2) atoms differ. The Eu(1) atom coordinates seven O atoms of one Pfbz anion bound via the chelate mode and five Pfbz anions bound via the monodentate mode, as well as two water molecules. The Eu(2) atom coordinates seven O atoms of two Pfbz anions bound via the chelate mode and five Pfbz anions bound via the monodentate mode. The Eu atoms are linked between each other by two bridging Pfbz anions and two O atoms of two chelate bridging Pfbz anions. The environment of the Eu atoms (EuO_9) corresponds to the “muffin” geometry, and the environment of the Cd atom (CdO_6N) corresponds to a one-capped trigonal prism. Selected bond lengths and angles are presented in Table 5.

The water molecule coordinated to the Eu atom participates in hydrogen bonding with two N atoms of the solvate Etypy and MeCN molecules (N...H 1.918–2.307, N...O 2.717, 2.898 Å, angle N...H–O 148.93° and 166.07°, respectively) (Fig. 4b).

Stacking interactions between the aromatic fragments of two coordinated Pfbz anions of the adjacent polymeric chains and solvate Etypy molecule (the distance between the centers of the interacting units and the angle between the planes are 3.52 Å, 3.23° and 3.55 Å, 5.21°, respectively) and between the aromatic fragments of the Pfbz anions inside one polymeric chain (the distance between the planes and the angle between the planes are 3.60 Å and 1.23°, respectively) (Fig. 4b) are observed in the packing of complex **VI**. The hydrogen atoms of the acetylene fragment and pyridine ring of the coordinated and solvate Etypy

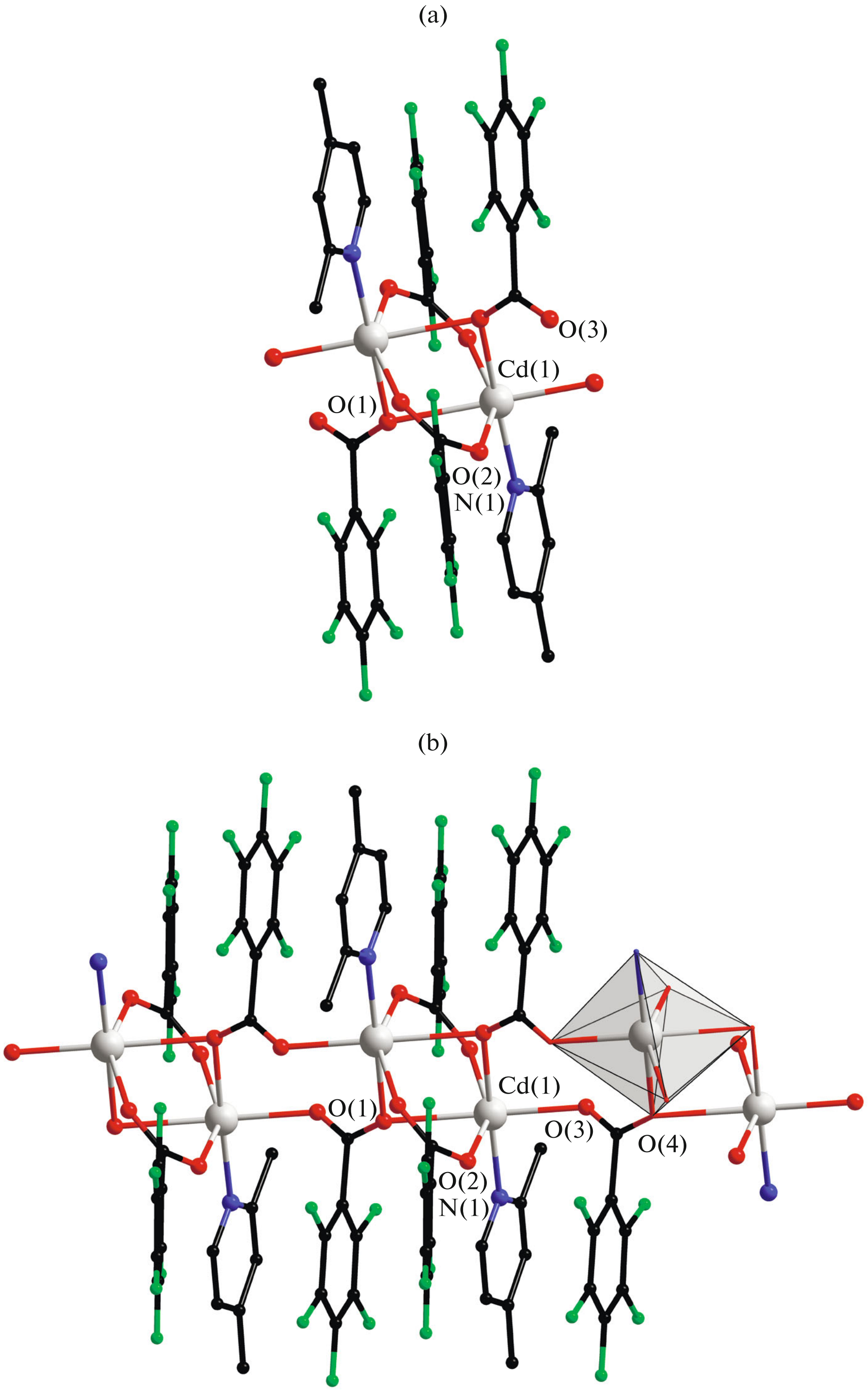


Fig. 3. (a) Binuclear fragment $\{Cd_2(O_2CC_6F_5)_4(Lut)_2\}$ and (b) polymeric chain of complex **V**. Hydrogen atoms are omitted.

molecules are involved in the formation of weak C–H...F contacts with the fluorine atoms of the Pfbz anions of one chain or between the adjacent polymeric chains (C–H...F–C 2.420–2.628 Å, angle C–H...F 111.3°–168.1°).

Unlike molecular complexes **III** and **IV**, polymer **VI** exhibits a considerable deviation of the geometry of the metal framework from linearity (angles CdEuEu for **VI** 110.85° and 111.45°), whereas the geometry of the metal framework is close to linear (CdEuEu

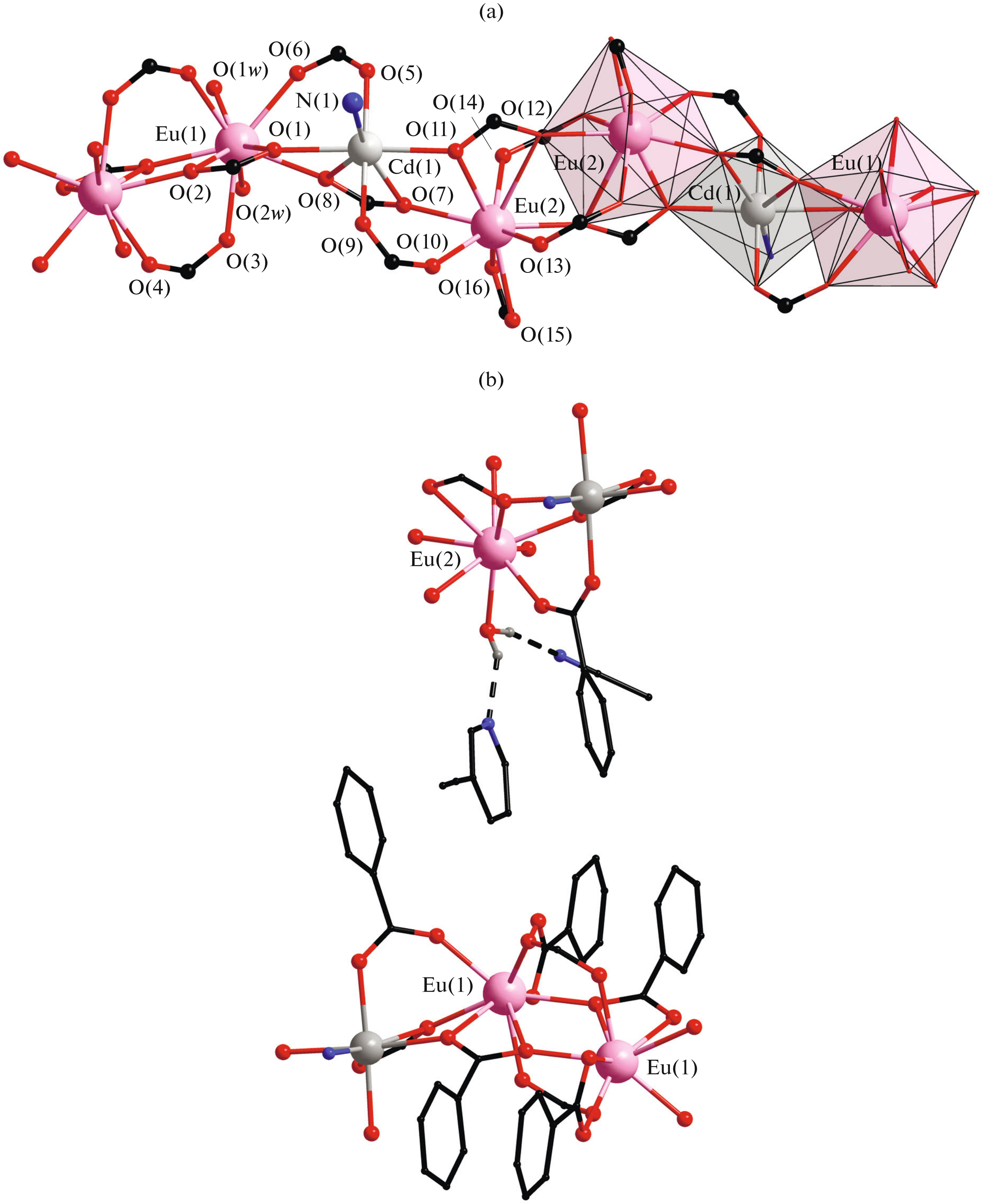


Fig. 4. Fragments of the (a) polymeric chain and (b) packing of complex **VI**. Only the hydrogen atoms involved in hydrogen bonding are shown. Fluorine atoms are omitted. The substituents at the carboxyl group (Fig. 1a) are omitted, and only the substituents at the carboxyl groups involved in inter- and intramolecular interactions are shown (Fig. 1b).

168.38° and 172.80°) for molecular complexes **III** and **IV**. It is most likely that the intra- and intermolecular π–π interactions lead to the distortion of the geometry of the metal framework of complex **VI**, whereas no stacking is observed in the crystals of compounds **III** and **IV** close to linear.

Only crystals of complex **VII** were isolated in the reactions of compounds **I** and **II** with Iquin. Complex

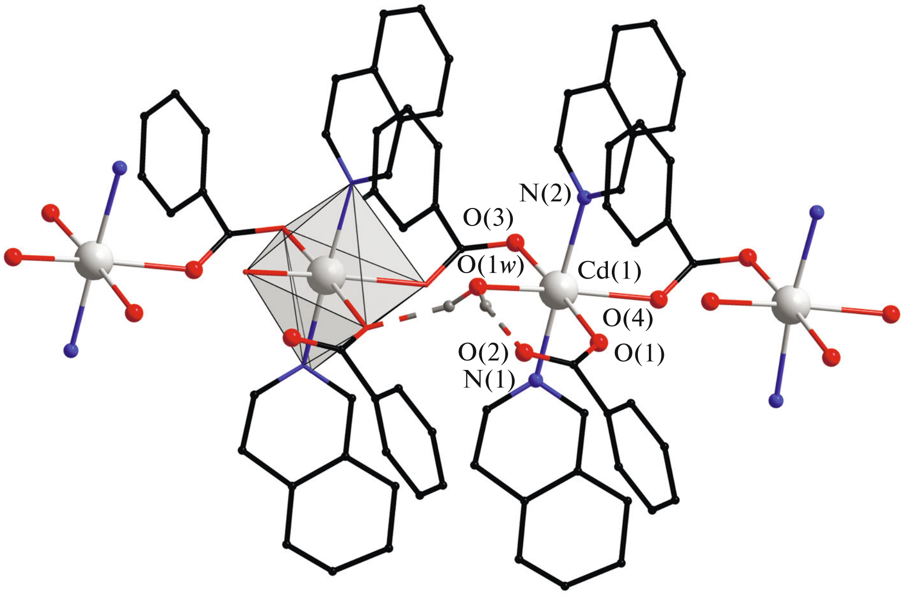


Fig. 5. Fragment of the polymeric chain of complex **VII**. Only the hydrogen atoms involved in hydrogen bonding are shown. Fluorine atoms are omitted.

VII crystallizes in the monoclinic crystal system with the space group $P2_1/c$. The cadmium atoms are bound in pairs by the bridging Pfbz anion to form the linear polymeric chain (Fig. 5). The metal center builds up its environment to the octahedral one (CdO_5N) by the coordination of the O atoms of the Pfbz anion bound via the monodentate mode, one water molecule, and two N atoms of two Iquin molecules. Selected bond lengths and distances are presented in Table 4.

The coordinated water molecule participates in hydrogen bonding with two O atoms of two Pfbz anions bound via the monodentate mode (O...O 2.658, 2.729, O...H 1.843, 1.949 Å, angle OHO 160.73° and 151.85°). The hydrogen atoms of the coordinated isoquinoline molecule are involved in the formation of weak C–H...F contacts with the fluorine atoms of the Pfbz anions of the adjacent polymeric chains (C–H...F 2.417–2.645, C..F 1.333–1.339 Å, angles CHF 114.65°–156.92°).

All carboxylate complexes with isoquinoline described in the literature $\{M^{x+}(O_2CR)_x(Iquin)_y\}$ have molecular structures, and no formation of polymers occurs (with ions of copper(II) [41], Ni(II) [42, 43], Co(II) [44, 45], and Cd(II) ($[Cd(O_2CR)_2(Iquin)_3]$ [39]).

The isolated and structurally characterized mononuclear cadmium(II) complex **VIII** that crystallizes in the monoclinic crystal system with the space group $C2/c$ also contains chelating Biquin. In the symmetric molecule of the complex (the C_2 axis passes through the Cd(1) atom and between the C(16) and C(16*A*) carbon atoms), the metal atom builds up its environment (CdN_2O_4) to a trigonal prism by the coordination of two Pfbz anions bound via the chelate mode and two N atoms of the chelate Biquin molecule (Fig. 6a). Supramolecular chains formed due to intermolecular interactions between both the aromatic Biquin fragments (the distance and angle between the planes are 3.50 Å and 0.00°, respectively) and Pfbz anions (the shortest distance and angle between the planes are 3.57 Å and 5.52°, respectively) (Fig. 6b) are formed in the crystal.

It is most likely that the formation of the mononuclear complex is related to the shielding of the metal center by the bulky chelating ligand.

In the case of 7,8-benzoquinoline, anionic polymer **IX** that crystallizes in the monoclinic space group $P2_1/c$ was isolated. The polymeric chain consists of the mononuclear fragments $\{Cd(Pfbz)_3\}^+$ linked to each other via one μ_2-O,O-bridging and two μ_2-O,O'-bridging Pfbz anions (Fig. 7). The protonated solvate molecule of the $HBquin^+$ ligand involved in the formation of the hydrogen bond with the uncoordinated oxygen atom of the Pfbz anion is the counterion of the polymeric chain (H...O 2.749, N...O 2.747 Å, angle NHO 162.8°).

The obtained result is unusual, since ionic compounds based on the mononuclear or binuclear anionic carboxylate complex and the corresponding quantity of organic cations are formed, as a rule, in the case of similar composition [46–49].

The packing of complex **IX** exhibits that the orientation of the Pfbz anions and solvate $HBquin^+$ molecules (Fig. 7, the distance between the centers of interacting units and the angle between the planes are

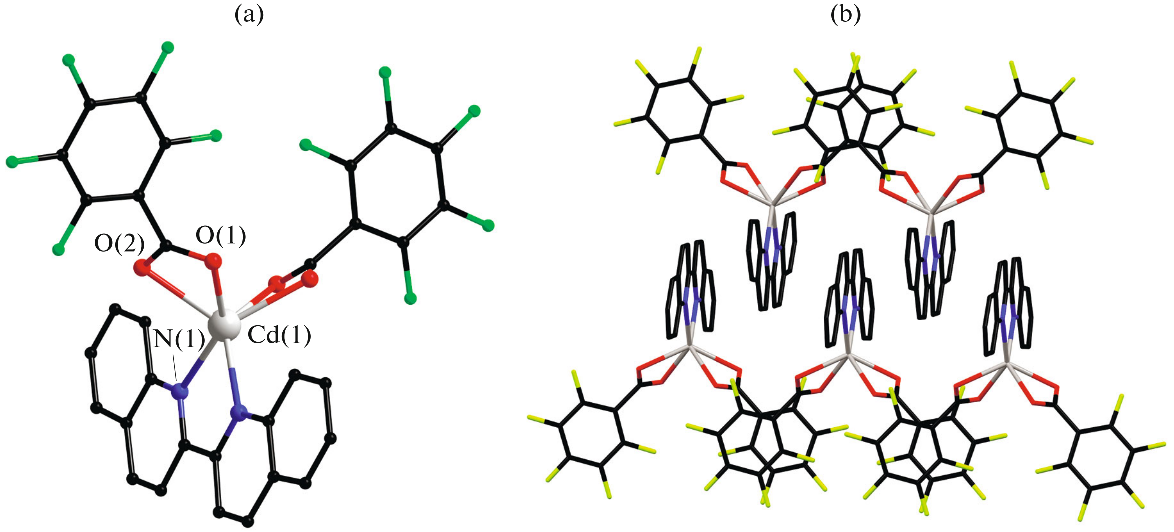


Fig. 6. (a) Structure of the molecule and (b) fragment of the crystal packing of complex **VIII**. Hydrogen atoms are omitted.

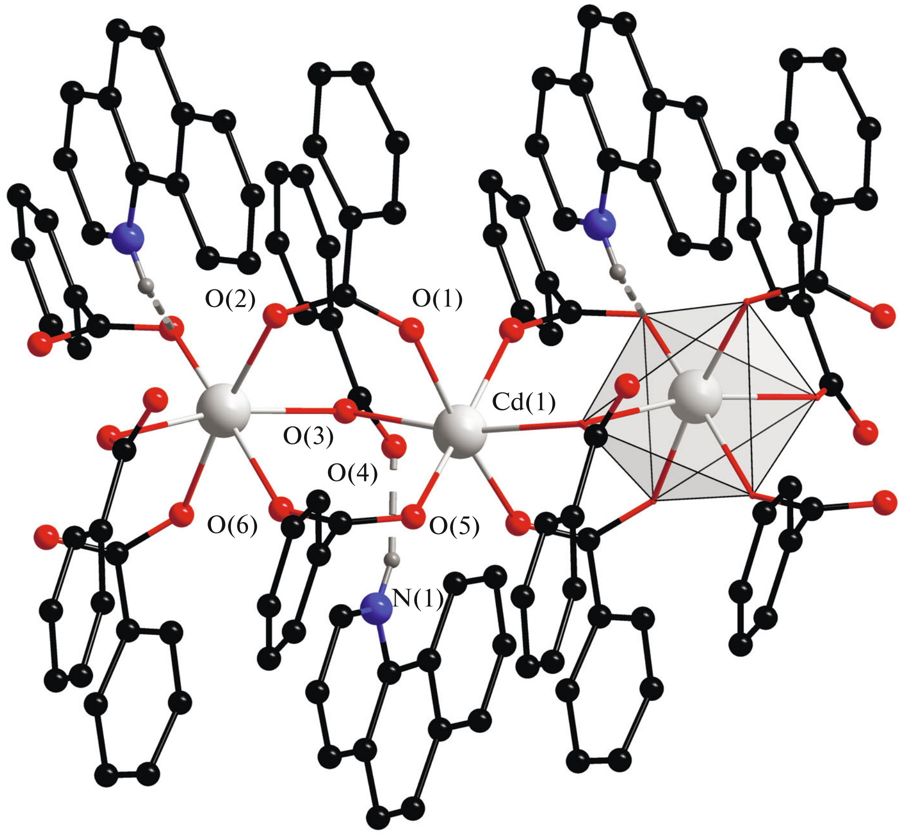


Fig. 7. Fragment of the polymeric chain of complex **IX**. Hydrogen atoms involved in hydrogen bonding are shown. Fluorine atoms are omitted.

3.56 Å and 6.40°, respectively) and of the pairs of the Pfbz anions inside the polymeric chain (the distance between the centers of the interacting units and the angle between the planes are 3.59 Å and 5.76°, respectively) is close to parallel, which can indicate in favor of intramolecular stacking interactions. The hydrogen atom of the solvate HBquin molecule participates in the formation of weak C–H...F–C contacts with the fluorine atoms of the Pfbz anions of the adjacent polymeric chains (C...F 1.341–1.344, H...F 2.618, 2.620, 2.646 Å, angle CHF 121.82°, 157.86°, 171.27°, respectively).

The obtained series of compounds shows a diversity of structures with cadmium(II) ions and pentafluorobenzoic acid anions in which the N-donor ligand is a factor determining the structure of the complex. The structural distinctions are observed for the carboxylate complexes of cadmium and divalent 3*d* metals (of the Fe–Zn series) with the monodentate pyridine derivatives for which, as a rule, the mono-, bi-, or trinuclear complexes are formed.

The tendency to form intramolecular stacking interactions between the C_6F_5 and C_6F_5 fragments and pyridine fragments of the coordinated ligands is shown using the synthesized complexes as an example. The tendency of forming intramolecular interactions is retained on going from the cadmium polymers to the Cd–Eu heterometallic tetranuclear and polymeric complexes.

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