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Influence of the Fluorinated Aromatic Fragments on the Structures of the Cadmium and Zinc Carboxylate Complexes Using Pentafluorobenzoates and 2,3,4,5-Tetrafluorobenzoates as Examples

M. A. Shmelev[a, *], G. N. Kuznetsova[a], F. M. Dolgushin[a, b], Yu. K. Voronina[a], N. V. Gogoleva[a], M. A. Kiskin[a], V. K. Ivanov[a], A. A. Sidorov[a], and I. L. Eremenko[a, b]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119992 Russia*
[b] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia*
**e-mail: shmelevma@yandex.ru*

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Abstract—A series of the cadmium and zinc carboxylate complexes with anions of pentafluorobenzoic (HPfbz) and 2,3,4,5-tetrafluorobenzoic (HTfbz) acids and N-donor ligands (1,10-phenanthroline (Phen) and quinoline (Quin)), $[Cd(Pfbz)_2(Phen)]_n$ (**I**), $[Cd(Pfbz)_2(Phen)_2]\cdot 2MeCN$ (**II**), $[Zn(H_2O)(Pfbz)_2(Phen)]$ (**III**), $[Zn_2Cd(Pfbz)_6(Phen)_2]\cdot 2C_6H_6$ (**IV**), $[Cd_2(H_2O)_2(Tfbz)_4(Phen)_2]$ (**V**), $[Cd_2(H_2O)_2(Tfbz)_4(Quin)_2]$ (**VI**), and $[Cd(Tfbz)_2(Phen)_2]\cdot HTfbz$ (**VII**), is synthesized. The structures of new complexes **I**–**VII** are determined by X-ray diffraction analysis (CIF files CCDC nos. 1871300, 2005461, 2005462, 2005464, 2005466, 2005465, and 2005459, respectively). The majority of the synthesized compounds is typical of intramolecular stacking interactions between the coordinated molecules of the aromatic N-donor ligands and fluorinated substituents of the carboxylate anions. These interactions lead to the formation of unusual compounds, which are different in the cases of pentafluorobenzoates and tetrafluorobenzoates, in particular, coordination polymer **I** and binuclear complexes **V** and **VI** with coordinated water molecules. The synthesized zinc and cadmium compounds differ in structure and composition.

Keywords: cadmium, zinc, pentafluorobenzoates, tetrafluorobenzoates, coordination polymers, stacking, X-ray diffraction analysis

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INTRODUCTION

The tasks of the synthesis of compounds with specified structures are related to both the molecular design and use of various types of noncovalent interactions (hydrogen and halogen bonds, stacking interactions, etc.) affecting the geometry and crystal packing of complexes [1–4]. Studies in this area can be aimed at searching for the factors providing the elimination of any type of weak interactions or, vice versa, the enhancement of them. The π–π interactions (stacking) between aromatic fragments of ligands can be distinguished among supramolecular effects. In the crystal structures of the compounds, this is reflected as a parallel or close to parallel arrangement of aromatic fragments at distances of 3.3–3.6 Å [5, 6].

The role of intramolecular and intermolecular π–π interactions between the aromatic systems was mentioned several times when describing the structures and crystal packings of the carboxylate complexes [7–11]. The formation of supramolecular, polymeric, or discrete structures was usually observed in the crystal, or an appreciable distortion of the geometry of molecules takes place in the case of intramolecular stacking.

It is known that the systems combining fluorine-substituted and nonfluorinated aromatic fragments in this or another way are typical of the parallel arrangement of all aromatic cycles and their approach to the distances shorter than 3.5 Å. For example, the packings of benzene and hexafluorobenzene are characterized by the same "ladder" type of the crystal packing, whereas the packing of cocrystallizate $C_6H_6\cdot C_6F_6$ is denser and more layered [12–14].

Only one similar coordination polymer of cadmium $[Cd(H_2O)(Pfbz)_2(Bipy)]_n$ (Bipy is 2,2'-bipyridine) [15] has previously been synthesized, which is a 1D coordination polymer, unlike the earlier described mononuclear and binuclear cadmium acetates ($[Cd(H_2O)(O_2CR)_2(Bipy)]$ and $[Cd_2(H_2O)_2(O_2CR)_4(Bipy)_2]$ [16, 17] with the similar ratio Cd : O_2CR : L = 1 : 2 : 1. The authors [16, 17] relate the stabilization of the polymeric structure to the C–H...F contacts, hydrogen bonds, and stacking interactions between the fluorinated and nonfluorinated aromatic fragments of coordinated Bipy and Pfbz. A similar stabilization of the polymeric structures is also observed for the cadmium pentafluorobenzoate complexes with the 2,4-lutidine and isoquinoline molecules in the anionic coordination polymer with the 7,8-benzoquinolinium cations [14]. It is important that the ligands containing the unsubstituted and perfluorinated aromatic substituents are simultaneously linked to the cadmium atoms in these compounds. In addition to the cross-coupling of aromatic fragments of this type, the use of the cadmium complexes was another factor providing the formation of a coordination polymer, since cadmium forms longer bonds with the atoms of its coordination environment compared to 3*d* metals.

The purpose of this work is to study the structures of the cadmium compounds formed by the cross-coupling of coordinated pentafluorobenzoate anions and 1,10-phenanthroline (Phen) molecules. The Phen molecule bound via the chelate mode has a condensed extended aromatic system providing favorable conditions for overlapping with the perfluorinated aromatic fragment. The cadmium 2,3,4,5-tetrafluorobenzoate complexes were synthesized to compare their properties with the unique properties of the perfluorinated aromatic fragments. The zinc complexes were synthesized to determine whether zinc forms the same compounds as cadmium.

EXPERIMENTAL

All procedures associated with the synthesis of new complexes were carried out in air using distilled water, ethanol (96%), acetonitrile (99.9%), and benzene (reagent grade). The following reagents were used to synthesize new compounds: $Cd(NO_3)_2 \cdot 4H_2O$ (99%, Acros organics), $Zn(NO_3)_2 \cdot 6H_2O$ (98%, Acros organics), KOH (analytical grade), HPfbz (99%, P&M Invest), HTfbz (98%, P&M Invest), 1,10-phenanthroline monohydrate (99%, Alfa Aesar), and quinoline (Quin, reagent grade). Compound $[\{Cd(Pfbz)(H_2O)_4^+\}_n \cdot n(Pfbz)^-]$ was synthesized according to an earlier described procedure [18] by the reaction of $Cd(OH)_2$ with HPfbz in water. Hydroxides $Zn(OH)_2$ and $Cd(OH)_2$ were synthesized by the reaction of stoichiometric amounts of KOH and $Zn(NO_3)_2 \cdot 6H_2O$ or $Cd(NO_3)_2 \cdot 4H_2O$ in water.

IR spectra were recorded on a Spectrum 65 (PerkinElmer) FTIR spectrophotometer using the attenuated total internal reflection (ATR) mode in a frequency range of 4000–400 cm^{-1}. Elemental analyses were carried out on a EuroEA 3000 CHNS analyzer (EuroVector).

Synthesis of $[Cd(Pfbz)_2(Phen)]_n$ (I). 1,10-Phenanthroline (0.060 g, 0.332 mmol) was added to a solution of compound $[\{Cd(Pfbz)(H_2O)_4^+\}_n \cdot n(Pfbz)^-]$ (0.200 g, 0.332 mmol) in MeCN (35 mL), and the mixture was stirred at 70°C for 7 min. A colorless solution was kept at room temperature with slow evaporation. Colorless crystals formed in 3 days and suitable for X-ray diffraction analysis (XRD) were decanted, washed with cold MeCN ($T \approx 5$°C), and dried in air. The yield of compound **I** was 0.154 g (64.8%) based on compound $[\{Cd(Pfbz)(H_2O)_4^+\}_n \cdot n(Pfbz)^-]$.

For $C_{26}H_8F_{10}N_2O_4Cd$

Anal. calcd., %	C, 43.7	H, 1.1	N, 3.9
Found, %	C, 44.1	H, 1.0	N, 3.9

IR (ATR, ν, cm^{-1}): 3059 w, 2292 w, 2252 m, 1621 w, 1594 m, 1546 m, 1490 s, 1471 m, 1427 s, 1374 s, 1343 s, 1290 s, 1223 w, 1141 m, 1101 m, 1039 s, 918 m, 879 m, 845 m, 814 m, 772 m, 728 s, 689 m, 676 m, 637 w, 550 m, 425 w, 411 m.

Synthesis of $[Cd(Pfbz)_2(Phen)_2] \cdot 2MeCN$ (II) was carried out by a method similar to that for compound **I** using Phen (0.120 g, 0.664 mmol). Colorless crystals formed in 5 days and suitable for XRD were decanted, washed with cold MeCN ($T \approx 5$°C), and dried in air. The yield of compound **II** was 0.133 g (42.3%) based on compound $[\{Cd(Pfbz)(H_2O)_4^+\}_n \cdot n(Pfbz)^-]$.

For $C_{42}H_{22}F_{10}N_6O_4Cd$

Anal. calcd., %	C, 51.6	H, 2.3	N, 8.6
Found, %	C, 52.2	H, 2.5	N, 9.0

IR (ν, cm^{-1}): 3321 w, 3068 w, 2984 w, 1987 w, 1618 s, 1590 s, 1514 s, 1484 s, 1425 s, 1357 s, 1344 s, 1338 s, 1279 m, 1224 w, 1145 w, 1102 m, 1092 m, 1051 w, 986 s, 916 s, 848 s, 828 m, 811 w, 784 w, 775 w, 749 s, 739 m, 722 s, 692 m, 637 m, 581 m, 549 m, 505 w, 466 m.

Synthesis of $[Zn(H_2O)(Pfbz)_2(Phen)]$ (III). Compound HPfbz (0.322 g, 1.515 mmol) was added to a suspension of $Zn(OH)_2$ (0.075 g, 0.757 mmol) in water (25 mL), and the reaction mixture was stirred at 80°C to the complete dissolution of the reactants. A colorless solution was evaporated to dryness, and the formed precipitate was dissolved in MeCN (20 mL) at 70°C. A weighed sample of Phen (0.136 g, 0.757 mmol) was added to the reaction mixture, and the mixture was stirred at 70°C for 5 min. The resulting colorless solution was kept at room temperature with slow evaporation. Colorless crystals formed in 5 days and suitable for XRD were decanted, washed with cold MeCN ($T \approx 5$°C), and dried in air. The yield of compound **III** was 0.362 g (69.7%) based on $Zn(OH)_2$.

For $C_{26}H_{10}F_{10}N_2O_5Zn$

Anal. calcd., %	C, 45.5	H, 1.5	N, 4.1
Found, %	C, 45.2	H, 1.3	N, 4.1

IR (ν, cm^{-1}): 3437 m, 3036 w, 1645 m, 1604 m, 1551 s, 1528 s, 1476 m, 1338 s, 1296 m, 1142 w, 1120 m, 988 s, 939 m, 808 m, 774 s, 713 m, 672 m, 607 m, 513 s, 488 m, 459 w.

Synthesis of $[Zn_2Cd(Pfbz)_6(Phen)_2]\cdot 2C_6H_6$ (IV). Compound HPfbz (0.322 g, 1.515 mmol) was added to a suspension of $Zn(OH)_2$ (0.075 g, 0.757 mmol) in water (25 mL), and the reaction mixture was stirred at 80°C to the complete dissolution of the reactants. The resulting colorless solution was evaporated to dryness, and the formed precipitate was dissolved in MeCN (30 mL) at 70°C. A weighed sample of $[\{Cd(Pfbz)(H_2O)_4^+\}_n \cdot n(Pfbz)^-]$ (0.456 g, 0.757 mmol) was added to the reaction mixture, the mixture was stirred at 70°C to the dissolution of the initial reactants, C_6H_6 (10 mL) and Phen (0.136 g, 0.757 mmol) were added, and the mixture was stirred at 70°C for 10 min. A colorless solution was kept at room temperature with slow evaporation. Colorless crystals formed in 8 days and suitable for XRD were decanted, washed with cold C_6H_6 ($T \approx 5$°C), and dried in air. The yield of compound **IV** was 0.824 g (53.7%) based on $Zn(OH)_2$.

For $C_{78}H_{28}F_{30}N_4O_{12}Zn_2Cd$

Anal. calcd., %	C, 46.2	H, 1.4	N, 2.8
Found, %	C, 46.6	H, 1.3	N, 2.9

IR (ν, cm^{-1}): 2988 w, 1623 s, 1521 s, 1488 s, 1429 s, 1379 s, 1283 m, 1225 m, 1146 w, 1107 s, 990 s, 928 m, 870 m, 845 m, 822 m, 768 m, 744 s, 726 s, 705 m, 644 m, 612 m, 584 w, 507 m.

Synthesis of $[Cd_2(H_2O)_2(Tfbz)_4(Phen)_2]$ (V). Compound HTfbz (0.133 g, 0.685 mmol) was added to a suspension of $Cd(OH)_2$ (0.050 g, 0.342 mmol) in water (20 mL), and the mixture was stirred at 80°C to the complete dissolution of the reactants. The obtained colorless solution was evaporated to dryness, the formed precipitate was dissolved in MeCN (15 mL) at 70°C, Phen (0.062 g, 0.342 mmol) was added to the obtained solution, and the mixture was stirred at 70°C for 5 min. A colorless solution was kept at room temperature with slow evaporation. Colorless crystals formed in 2 days and suitable for XRD were decanted, washed with cold MeCN ($T \approx 5$°C), and dried in air. The yield of compound **V** was 0.122 g (51.2%) based on $Cd(OH)_2$.

For $C_{52}H_{24}F_{16}N_4O_{10}Cd_2$

Anal. calcd., %	C, 44.8	H, 1.7	N, 4.0
Found, %	C, 45.1	H, 2.0	N, 4.0

IR (ν, cm^{-1}): 3304 s, 3065 m, 2975 m, 1980 w, 1579 s, 1516 s, 1471 s, 1424 m, 1374 s, 1345 s, 1322 m, 1286 m, 1260 m, 1222 w, 1998 w, 1181 w, 1143 w, 1095 s, 1029 s, 909 s, 896 m, 863 m, 844 s, 803 m, 772 s, 759 s, 727 m, 720 m, 710 s, 692 s, 635 m, 626 m, 521 w, 496 w, 469 w.

Synthesis of $[Cd_2(H_2O)_2(Tfbz)_4(Quin)_2]$ (VI) was similar to the synthesis of compound **V** using Quin (0.116 mL, 1.027 mmol) instead of Phen. Colorless crystals formed in 3 days and suitable for XRD were decanted, washed with cold MeCN ($T \approx 5$°C), and dried in air. The yield of compound **VI** was 0.106 g (47.9%) based on $Cd(OH)_2$.

For $C_{46}H_{22}F_{16}N_2O_{10}Cd_2$

Anal. calcd., %	C, 42.8	H, 1.7	N, 2.2
Found, %	C, 42.6	H, 1.6	N, 2.3

IR (ν, cm^{-1}): 3080 m, 1719 m, 1578 s, 1518 s, 1473 s, 1391 s, 1359 s, 1350 s, 1322 m, 1286 w, 1262 m, 1254 m, 1224 m, 1202 m, 1143 m, 1096 m, 1025 s, 908 m, 883 w, 864 m, 802 m, 795 s, 771 m, 759 m, 752 s, 686 m, 639 m, 617 w, 555 w, 521 w, 469 w, 455 w.

Synthesis of $[Cd(Tfbz)_2(Phen)_2]\cdot HTfbz$ (VII) was similar to the synthesis of compound **V** using Phen (0.124 mg, 0.684 mmol). Colorless crystals formed in 8 days and suitable for XRD were decanted, washed with cold MeCN ($T \approx 5$°C), and dried in air. The yield of compound **VII** was 0.158 g (32.9%) based on HTfbz.

For $C_{45}H_{20}F_{12}N_4O_6Cd$

Anal. calcd., %	C, 51.3	H, 1.8	N, 5.3
Found, %	C, 51.7	H, 2.0	N, 5.5

IR (ν, cm^{-1}): 3079 m, 2972 m, 1952 w, 1728 w, 1684 m, 1574 s, 1523 s, 1500 m, 1476 s, 1430 m, 1388 s, 1338 m, 1315 m, 1288 w, 1244 w, 1230 w, 1195 m, 1162 w, 1147 w, 1118 w, 1028 s, 951 m, 913 s, 863 m, 807 s, 799 m, 784 s, 750 s, 729 m, 703 s, 688 m, 627 m, 610 m, 565 w, 520 w, 481 m, 470 w.

XRD of single crystals of compounds **I**–**VII** was carried out on a Bruker Apex II diffractometer or a Bruker Apex II DUO diffractometer equipped with a CCD detector (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator) [19]. A semiempirical absorption correction was applied for all compounds using the SADABS program [20]. The structures were solved by direct methods and refined by full-matrix least squares in the anisotropic approximation for all nonhydrogen 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 by the SHELX program package [21] using OLEX 2 [22]. The geometry of the polyhedra of the metals was determined using the SHAPE 2.1 program [23, 24]. The crystallographic parameters and structure refinement details for compounds **I**–**VII** are presented in Tables 1 and 2. Selected distances and angles for compounds **I**–**VII** are given in Tables 3 and 4. Selected distances and angles of intra- and intermo-

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

Parameter	Value		
	I	**II**	**III**
FW	714.74	977.07	685.73
T, K	120(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$
a, Å	24.0270(15)	16.9021(7)	10.7251(5)
b, Å	13.3587(9)	10.0614(5)	11.1900(4)
c, Å	7.4456(5)	24.1962(12)	11.6845(4)
α, deg	90	90	75.3920(10)
β, deg	95.4295(13)	103.918(2)	79.511(2)
γ, deg	90	90	65.2760(10)
V, Å^3	2379.1(3)	3994.0(3)	1227.90(8)
Z	4	4	2
ρ_{calc}, g cm^3	1.995	1.625	1.855
μ, mm^{-1}	1.037	0.645	1.121
θ_{max}, deg	27.997	26.000	30.03
T_{min}/T_{max}	0.761/0.922	0.685/0.746	0.649/0.746
Number of measured reflections	18016	37974	16251
Number of independent reflections	2786	7840	7387
Number of reflections with $I > 2\sigma(I)$	2758	5988	5776
R_{int}	0.0221	0.0606	0.0485
Number of refined parameters	9858	2843	6142
GOOF	1.094	1.059	1.028
R_1 ($I > 2\sigma(I)$)	0.0176	0.0513	0.0488
wR_2 ($I > 2\sigma(I)$)	0.0451	0.1308	0.1171
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	–0.255/0.710	–0.757/0.707	–0.350/0.373

lecular interactions for compounds **I–VII** are presented in Tables 5 and 6.

The coordinates of atoms and other parameters of compounds **I–VII** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1871300, 2005461, 2005462, 2005464, 2005466, 2005465, and 2005459, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The starting cadmium compound was $[\{Cd(Pfbz)(H_2O)_4^+\}_n \cdot n(Pfbz)^-]$ [18], the reaction of which with

Table 2. Crystallographic parameters and structure refinement details for compounds **IV**–**VII**

Parameter	Value			
	IV	**V**	**VI**	**VII**
FW	2026.18	1393.55	1291.45	1053.05
T, K	296(2)			
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	13.1039(8)	8.533(19)	8.169(5)	22.5145(14)
b, Å	16.3964(10)	10.45(2)	12.183(7)	7.9644(4)
c, Å	17.8982(13)	14.72(4)	12.299(8)	23.1560(15)
α, deg	83.418(3)	77.20(9)	75.68(2)	90
β, deg	75.851(3)	86.06(11)	74.99(2)	104.127(2)
γ, deg	82.578(3)	76.95(7)	86.64(2)	90
V, Å^3	3683.8(4)	1247(5)	1145.5(12)	4026.6(4)
Z	2	1	1	4
ρ_{calc}, g cm^3	1.827	1.855	1.872	1.737
μ, mm^{-1}	1.076	0.978	1.055	0.656
θ_{max}, deg	28.395	25.997	30.16	25.998
T_{min}/T_{max}	0.593/0.746	0.448/ 0.746	0.902/0.949	0.968/ 0.993
Number of measured reflections	37985	8972	15869	19560
Number of independent reflections	18545	4790	4466	7865
Number of reflections with $I > 2\sigma(I)$	9598	3701	4117	5079
R_{int}	0.0471	0.0438	0.0664	0.0758
Number of refined parameters	4180	4521	6036	3870
GOOF	0.947	1.042	0.982	0.971
R_1 ($I > 2\sigma(I)$)	0.0528	0.0823	0.0422	0.0552
wR_2 ($I > 2\sigma(I)$)	0.1182	0.2207	0.1223	0.1214
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	−1.989/0.785	−1.069/1.751	−0.924/1.067	−0.486/0.435

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

Bond	*d*, Å				
	I	**II**	**V**	**VI**	**VII**
Cd–N(L)	2.366(1)	2.387(3)–2.459(3)	2.403(8), 2.428(8)	2.352(3)	2.343(4)–2.449(4)
Cd–O(H_2O)			2.298(7)	2.332(3)	
Cd–O(O_2CR)	2.425(1)–2.466(1)	2.281(3)–2.609(4)	2.241(8)–2.551(8)	2.325(3)–2.500(4)	2.219(3), 2.383(3)
Cd...Cd	4.008(3)	9.728(1)	4.043(7), 5.569(12)	4.160(2), 5.174(3)	7.9644(4)
Angle	ω, deg				
CdCdCd		136.48(2)			

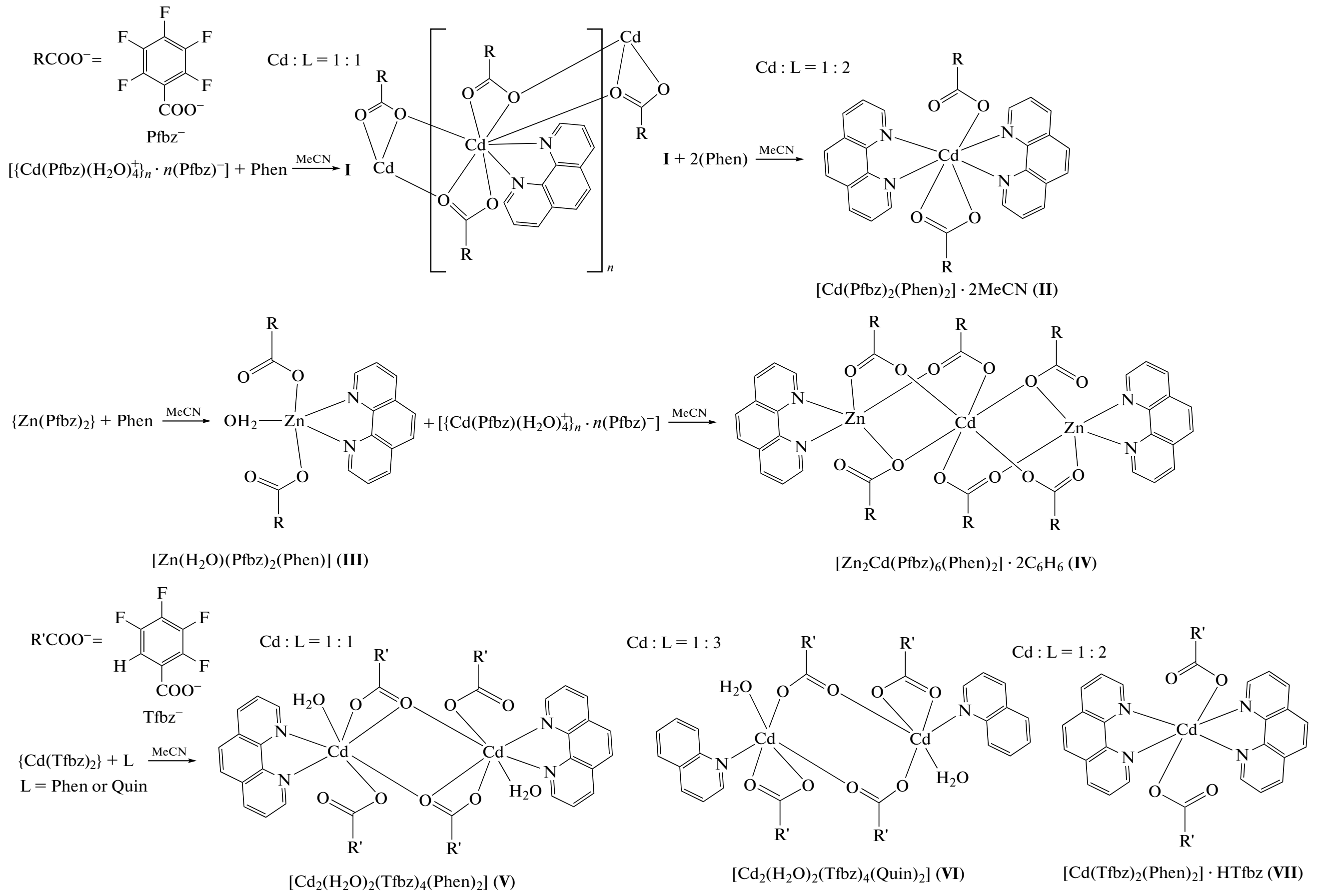
Table 4. Selected geometric characteristics of complexes **III** and **IV**

Bond	*d*, Å	
	III	**IV**
Zn–N(Phen)	2.103(2), 2.160(2)	2.073(3), 2.149(3)
Zn–O(H_2O)	2.028(2)	
Zn–O(O_2CR)	1.991(2), 2.058(2)	2.015(3)–2.045(2)
Cd–O(O_2CR)		2.240(2)–2.317(3)
Zn...Cd		7.111(7)
Zn...Zn	6.663(7)	3.541(6)
Angle	ω, deg	
ZnCdZn		177.76(2)

Phen affords coordination polymer **I** or molecular complex **II**, depending on the ratio Cd : Phen = 1 : 1 or 1 : 2, respectively. At the stoichiometric ratio of the initial reagents zinc forms molecular mononuclear complex **III**. The reaction of $Zn(Pfbz)_2$ (obtained *in situ*) followed by the addition of $[\{Cd(Pfbz)(H_2O)_4^+\}_n{\cdot}n(Pfbz)^-]$ and Phen (Zn : Cd : Phen = 1 : 1 : 1) gave heterometallic complex **IV**. In the case of 2,3,4,5-tetrafluorobenzoates, molecular complexes **V**, **VI**, and **VII** were obtained. The syntheses and structures of complexes **I**–**VII** are presented in Scheme 1.

Table 5. Geometric parameters of hydrogen bonds and contacts C–H...F in the crystal of compounds **I**–**VII**

Hydrogen bond	Distance, Å			D – H–A, deg
	D–H	H...A	D...A	
		I		
C(8)–H(8A)...F(3)	0.95	2.52	3.417(2)	158
C(10)–H(10A)...F(6)	0.95	2.47	3.416(2)	175
		II		
C(1B)–H(1BA)...F(14A)	1.10	2.48	3.36(2)	137
C(1D)–H(1DA)...F(12A)	1.10	2.33	3.16(3)	131
C(1D)–H(1DB)...F(10A)	1.10	2.17	3.26(2)	169
C(16)–H(16)...F(14B)	0.93	2.53	3.44(2)	168
C(1D)–H(1DB)...F(11A)	1.10	2.49	3.20(2)	121
C(1D)–H(1DB)...F(10B)	1.10	2.37	3.44(2)	163
		III		
O(1)–H(1A)...O(3)	0.82(4)	1.91(4)	2.724(3)	172(4)
O(1)–H(1B)...O(5)	0.93(3)	1.70(3)	2.601(3)	162(3)
C(11)–H(6)...F(4)	0.93	2.43	3.243(4)	146
		IV		
C(50)–H(50)...F(14)	0.93	2.39	3.145(4)	139
C(72)–H(72)...F(11)	0.93	2.47	3.244(6)	138
C(74)–H(74)...F(28)	0.93	2.45	3.100(4)	127
		V		
O(5)–H(5A)...O(1)	0.91	1.89	2.710(11)	148
O(5)–H(5B)...O(4)	0.92	1.83	2.735(13)	169
C(19)–H(19)...F(5)	0.93	2.52	3.214(17)	132
		VI		
O(5)–H(5A)...O(2)	0.87	1.88	2.720(7)	163
O(4S)–H(5B)...O(3)	0.87	2.21	2.910(6)	137
		VII		
O(5)–H...O(2)	0.82	1.77	2.555(5)	161
C(34)–H(34)...F(11)	0.93	2.39	2.795(9)	106
C(38)–H(38)...F(12A)	0.93	2.55	3.374(8)	148



Scheme 1.

We used Phen to increase the probability of forming intermolecular interactions in the crystal of the complexes, since a higher tendency for its participation in the formation of intermolecular interactions in the crystal packings than in the complexes with Bipy is observed [6]. Compound **I** (Fig. 1) is built of equivalent symmetric (2-fold axis passes through the cadmium atom) mononuclear fragments {Cd(Pfbz)$_2$-(Phen)}. The Cd atoms are bound by the chelate-bridging pentafluorobenzoate anions in such a way that two anions of four carboxylate anions coordinated by each Cd atom form the chelate cycle with the metal. Each metal atom builds up its environment by the coordination of the N atoms of the Phen molecule to a square antiprism (CdN_2O_6). The main distances and angles of complex **I** are presented in Table 3.

The parallel orientation of all aromatic fragments Pfbz and Phen inside one polymeric chain is observed in the crystal of complex **I**, which possibly indicates the presence of stacking interactions. This arrangement of the aromatic fragments leads, most likely, to metal center deblocking and creates favorable conditions for the formation of the coordination polymer. Probably, the stabilization of the polymeric structure is related to the stacking interactions of the coordinated Phen molecules and pentafluorophenyl substituents inside the chain. The hydrogen atoms of the Phen molecules are involved in the C–H...F contacts with the fluorine atoms of the Pfbz anions of three adjacent polymeric chains. Selected distances and angles of intra- and intermolecular interactions of complex **I** are presented in Tables 5 and 6.

The use of Phen results in the formation of a “denser” packing of the polymer compared to the described compound $[Cd(H_2O)(Pfbz)_2(Bipy)]_n$ [15], where the metal atoms are bound by only one bridging Pfbz anion and the distance between them is 5.079 Å versus 4.008 Å in the case of compound **I**.

Compound **I** retains its composition and structure upon recrystallization from ethanol or benzene.

It is known that the cadmium complexes with anions of monocarboxylic acids and 1,10-phenanthroline $[Cd(O_2CR)_2(Phen)]$ are characterized by the formation of molecular structures [25–31]. The 2,4,5-trifluorobenzoate, 2-fluorobenzoate, and benzoate complexes of cadmium with the geometric characteristics very close to those of the pentafluorobenzoate anion and exactly the same composition as that of compound **I** are binuclear molecular complexes [26, 29]. The cadmium complexes with anions of

Table 6. The π...π interactions in the crystal packings of complexes **I**–**VII**

Interaction	Cg–Cg*, Å	Cg–Perp*, Å	α, deg	β, deg	γ, deg
			I		
Phen–Pfbz	3.782(9)	3.241(6)	9.78(7)	21.8	31.1
			II		
Phen–Phen	3.885(3)	3.408(2)	1.1(3)	28.7	28.7
Phen–Phen	3.797(3)	3.456(2)	1.4(3)	24.7	24.4
			III		
Phen–Pfbz	3.752(2)	3.528(1)	4.32(13)	19.9	19.9
Phen–Phen	3.640(1)	3.416(1)	1.69(10)	12.3	12.1
			IV		
Phen–C_6H_6	3.792(3)	3.6683(17)	10.1(3)	13.1	14.7
Phen–C_6H_6	3.704(3)	3.4543(10)	9.3(2)	20.9	12.1
			V		
Phen–Pfbz	3.506(11)	3.424(5)	15.5	12.4	6.5(4)
Phen–Pfbz	3.456(11)	3.423(5)	2.1	7.9	6.5(5)
Phen–Phen	3.491(11)	3.461(3)	7.6	7.4	0.3(4)
			VI		
Quin–Hfbz	3.845(5)	3.536(3)	17.8	23.2	8.5(3)
Hfbz–Hfbz	3.571(5)	3.506(3)	0.0(4)	10.9	10.9
Quin–Quin	3.658(4)	3.540(3)	14.6	13.9	0.9(3)
			VII		
Phen–Phen	3.721(3)	3.405(2)	0.0(3)	23.8	23.8
Phen–Tfbz	3.810(3)	3.369(2)	6.7(2)	22.4	27.0
Phen–Tfbz	3.439(3)	3.284(2)	6.8(2)	10.6	17.3

* Cg is the centroid of the aromatic rings, and Perp is the perpendicular to the ring plane.

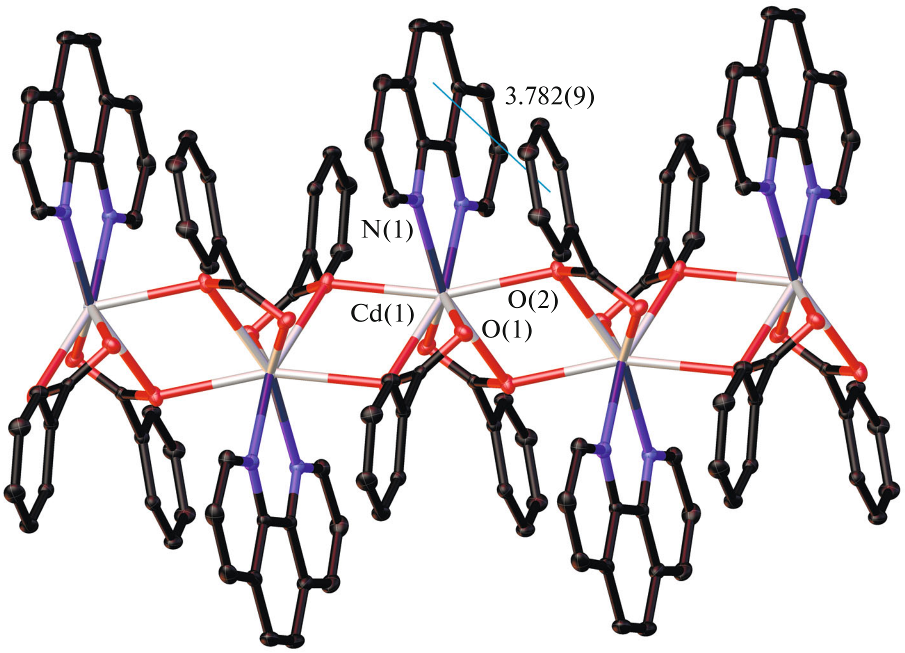


Fig. 1. Fragment of the polymeric chain of complex **I**. Hydrogen and fluorine atoms are omitted.

2-hydroxy-1-naphthoic, 1-naphthoic, and 6-hydroxy-1-naphthoic acids and Phen of a similar composition are also binuclear molecular complexes [28, 31, 32]. However, there are several polymeric structures for the cadmium complexes in which the Phen molecules are combined with diverse aromatic anions of monocarboxylic acids (2,4,6-trimethylbenzoic [33], 3-(2-furyl)acrylic [34], and 3,5-dimethylbenzoic [35] acids) of the composition $[Cd(RCOO)_2(Phen)]_n$ or $[Cd(H_2O)(RCOO)_2\text{-}(Phen)]_n$. The 2-furanacrylate polymer is built with the participation of the chelate-bridging carboxylate anions, the Cd...Cd distance corresponds to the minimum distance among the considered compounds (4.174 Å), and the adjacent coordination polyhedra of the metal atoms have a common edge. In the 3,5-dimethylbenzoate polymer, the adjacent cadmium atoms are also linked by two bridging carboxylate anions, but they do not form chelate cycles simultaneously and, hence, the coordination polyhedra of the adjacent Cd atoms have no common atoms and a more extended or “loosen” polymeric chain is observed. The 3,4,6-trimethylbenzoate polymer is formed by the cadmium atoms linked by only one bridging carboxylate anion, and the second carboxylate anion is bound via the monodentate mode to only one metal center, whose coordination environment is built by the water molecule. The maximally “extended” and probably least strongly bound polymer is formed in the crystal. However, the parallel orientation of the aromatic Phen fragments and monocarboxylic acid anion similar to that in compound **I** is observed just in this case.

The nuclearity of the complex changes with an increase in the amount of Phen in the coordination sphere of the cadmium atom. Compound **II** (Fig. 2) is mononuclear as the most part of the known carboxylate complexes with a similar composition [30, 36–46].

In the structure of complex **II**, the Cd atom builds up its environment to a one-capped octahedron by the coordination of the Pfbz anions bound via the chelate and monodentate modes and four N atoms of two Phen molecules (CdO_3N_4). Selected distances and angles of complex **II** are presented in Table 3.

An analysis of the crystal packing of compound **II** reveals that one of the coordinated Phen molecules is involved in stacking interactions with two aromatic Phen fragments of two adjacent molecules of the complex. The hydrogen atoms of Phen and solvate acetonitrile molecules are involved in the C–H...F contacts with the F atoms of the Pfbz anions. Selected distances and angles of intra- and intermolecular interactions in complex **II** are presented in Tables 5 and 6.

Complex **II** demonstrates unfavorable conditions for the formation of the polynuclear and polymeric structures, which is associated, most likely, with a decrease in the conformational mobility of the molecule and shielding of the metal center (or a sharp decrease in the possibility of deblocking of the metal center necessary for the formation of the polynuclear structure).

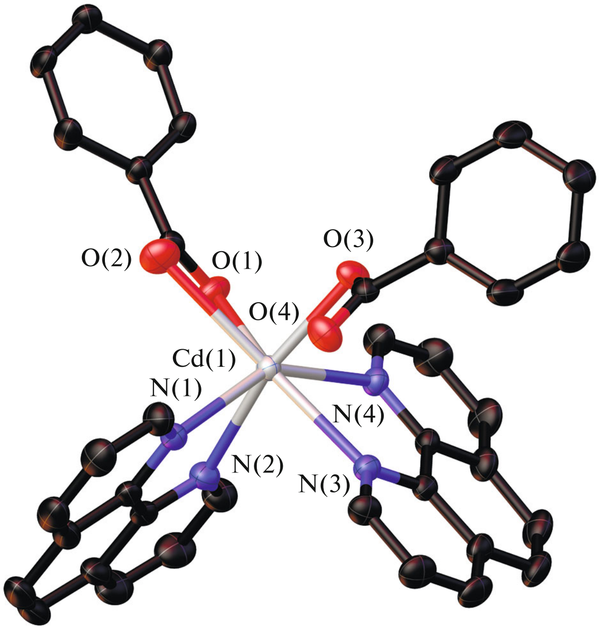


Fig. 2. Structure of complex **II**. Hydrogen and fluorine atoms and solvate molecules are omitted.

Under the crystallization conditions similar to the synthesis conditions of complex **I**, zinc forms no coordination polymers: we succeeded to isolate only mononuclear complex **III** (Fig. 3). In the structure of complex **III**, the Zn atom coordinates three oxygen atoms of two Pfbz anions of the water molecule bound via the monodentate mode and two N atoms of the Phen molecule thus building up its environment to a square pyramid (ZnO_3N_2, $\tau(Zn) = 0.1$). The mononuclear structure is typical of the $\{Zn(H_2O)\text{-}(Phen)(RCOO)_2\}$ complexes [47–50]. Selected bond lengths of complex **III** are presented in Table 4.

In the packing of complex **III**, the hydrogen atoms of the coordinated water molecules are involved in intra- and intermolecular hydrogen bonds with the O atoms of the Pfbz anions resulting in the dimerization of molecules of the complex (Fig. 3a). Similarly to compound **I**, stacking interactions of the Pfbz anions and aromatic rings of Phen of two adjacent molecules of complex **III** are observed. In addition, the crystal exhibits π–π interactions between Phen of two adjacent mononuclear fragments, and supramolecular stacks of the aromatic fragments Phen and Pfbz along the *b* axis are formed in the packing of complex **III** (Fig. 3b). The hydrogen atoms of the Phen molecules are involved in the intermolecular contacts C–H...F with the fluorine atoms of the Pfbz anions. The main distances and angles of intra- and intermolecular interactions in complex **III** are presented in Tables 5 and 6.

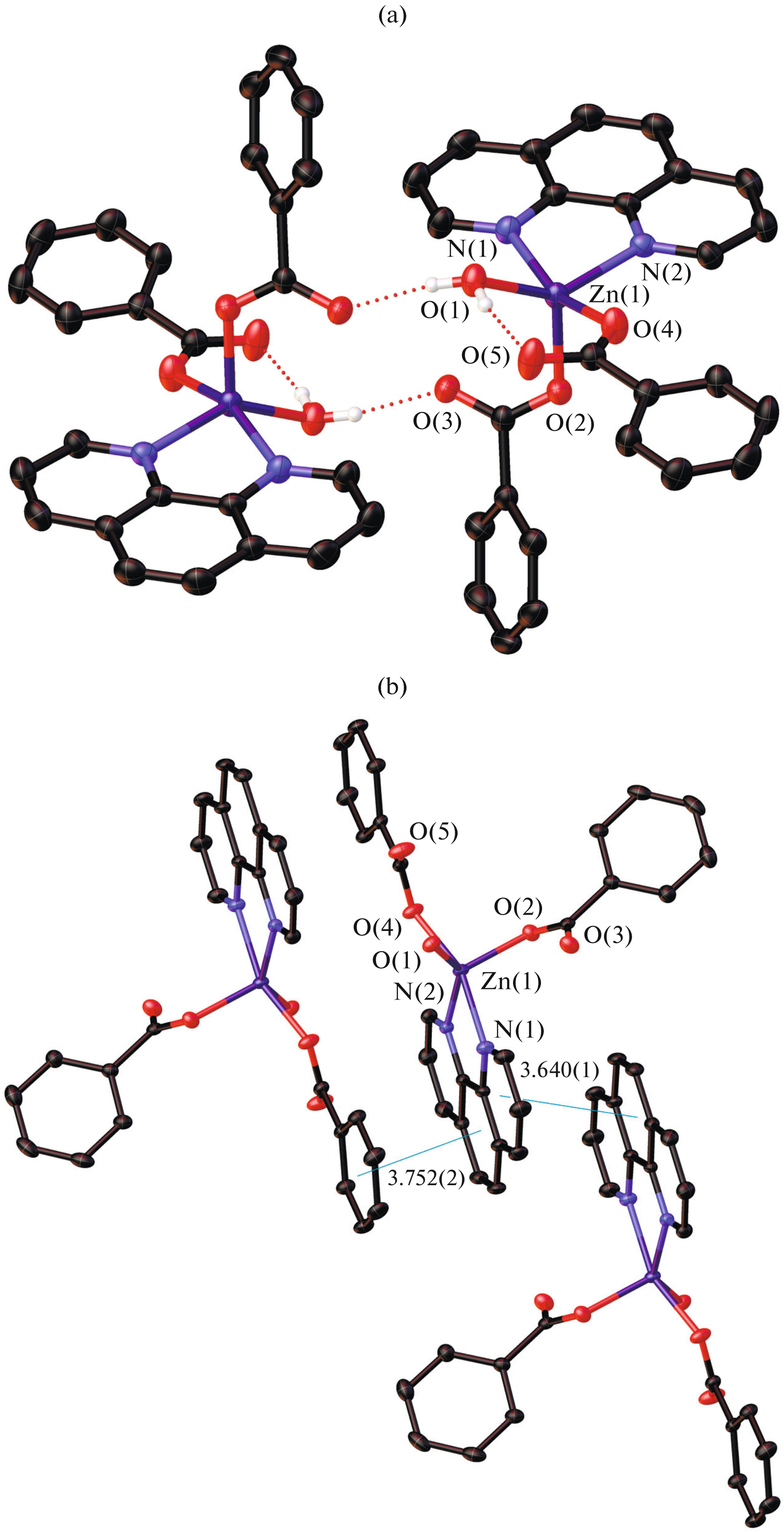


Fig. 3. Fragment of the crystal packing of complex **III**: (a) dimeric molecule and (b) supramolecular stacks of the Phen and Pfbz aromatic fragments along the *b* axis. Fluorine atoms are omitted. The hydrogen atoms involved in hydrogen bonding are shown.

Transparent gels prone to syneresis were formed on cooling of more concentrated solutions (the reaction mixture was evaporated to 5 mL) of compound **III**. The molecular structure of complex **III** seems to be quite regular and expected, while its ability to form gels in concentrated solutions of benzene, acetonitrile, and ethanol turned out to be rather unexpected. It can be assumed that associates and oligomers with the structural motif observed in the cadmium pentafluorobenzoate coordination polymer $[Cd(H_2O)(Pfbz)_2(Bipy)]_n$ can be formed in solutions [15].

The composition of complex **III** is similar to that of complex **I**, and its structure was analyzed in comparison with this compound. The superimposition of the structures of complexes **I** and **III** allowed us to reveal the following. Unlike the fragment of the polymeric chain of complex **I** where the Pfbz anions lie in the planes close to the Phen plane due to the intramolecular interactions and the angle between the planes of the Pfbz anions and Phen molecules is 9.87° and 10.18°, in the structure of mononuclear complex **III** the site of one of the Pfbz anions of complex **I** is occupied by the coordinated water molecule and the second Pfbz anion strongly deviates from the Phen plane (the angle between the planes is 75.43°) to block some coordination sites of the metal center (Fig. 4). In the case of complex **III**, the M...M distance increases significantly from 4.008(3) Å for complex **I** to 4.969(6) Å for complex **III**. This can be attributed to weaker intermolecular interactions and the influence of the water molecule coordinated by the zinc atom on the structure and crystal packing of complex **III**.

It is also interesting to compare compound **III** with the bipyridine complex $[Cd(H_2O)(Pfbz)_2(Bipy)]_n$ [15] of a similar composition. In spite of similar compositions, the structures of the complexes differ strongly already at the level of M–O(N) bond lengths and O(N)MO(N) bond angles. These distinctions are too significant to be explained by only the difference in atomic radii of zinc and cadmium. In particular, the maximum angle in the zinc complex is observed between Phen and Pfbz, whereas in the cadmium complex the maximum angle is observed between two Pfbz. In the zinc complex, the angles between the planes of the ligands are 3.55° and 75.87° between Phen and Pfbz and 73.99° between the Pfbz planes. In the cadmium complex, the angles between the planes of Bipy and Pfbz are 14.06° and 20.33°, and that between Pfbz is 31.46°. The angles between the centroids of the N-donor substituents and water are 121.83° in the zinc complex and 83.28° in the cadmium complex. Thus, the complexes are characterized by quite different geometric structures, which can be both a reason for and a consequence of the polymeric and molecular structures of these compounds.

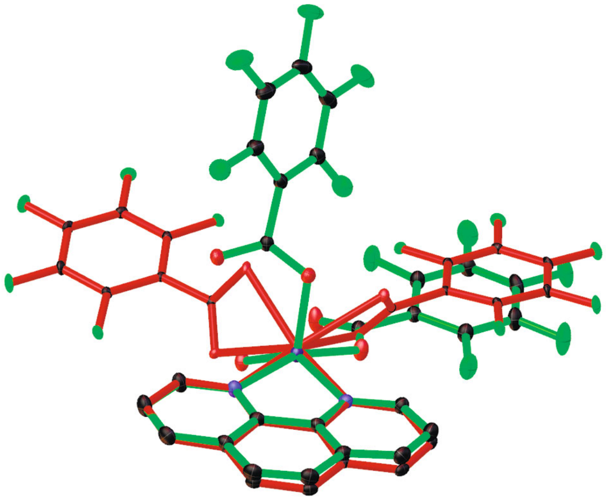


Fig. 4. Superimposition of the fragment of the polymeric chain of complex **I** (green) and the molecule of complex **III** (red). Hydrogen atoms are omitted. The carbon atoms in the structure of complex **I** are shown by balls.

We also studied the possibility of synthesizing a structural analogue of complex **I** by the substitution of 50% cadmium atoms by zinc atoms. An attempt to synthesize the heterometallic polymeric pentafluorobenzoate {ZnCd} complex with Phen and its crystallization from benzene gave molecular trinuclear compound **IV** (Fig. 5a). In the structure of compound **IV**, each terminal zinc atom is linked to the central cadmium atom in the octahedral environment by two bridging Pfbz anions and one bridging oxygen atom of the third Pfbz anion. The terminal zinc atoms build up their environment to an octahedron by the coordination of the N atoms of the Phen molecule. Selected bond lengths of complex **IV** are presented in Table 4.

Note that two similar trinuclear heterometallic complexes $\{Zn_2Cd(O_2CR)_6(L)_2\}$ with benzoic acid anions and 1,2-bipyridineethane [51] and with crotonic acid anions and quinoline [52] are known.

Solvate C_6H_6 molecules participate in stacking interactions simultaneously with the aromatic Phen fragments of two adjacent molecules of the complex to form supramolecular stacks parallel to the *ac* plane (Fig. 5b). The main geometric characteristics of intra- and intermolecular interactions in complex **IV** are presented in Tables 5 and 6.

The synthesis of compounds **I**, **III**, and **IV** shows that very unexpected structures can be formed in a zinc–cadmium system. A complete information about these structures can be obtained after further detailed studies.

As said above, the cadmium 2,4,5-trifluorobenzoate, 2-fluorobenzoate, and benzoate complexes with the same composition as that of complex **I** are binuclear molecular complexes [26, 29, 53]. We assumed that a boundary situation can take place in the case of the 2,3,4,5-tetrafluorobenzoate compounds. The structure and composition of the 2,3,4,5-tetrafluorobenzoate complex with Phen (**V**) (Fig. 6a) differed

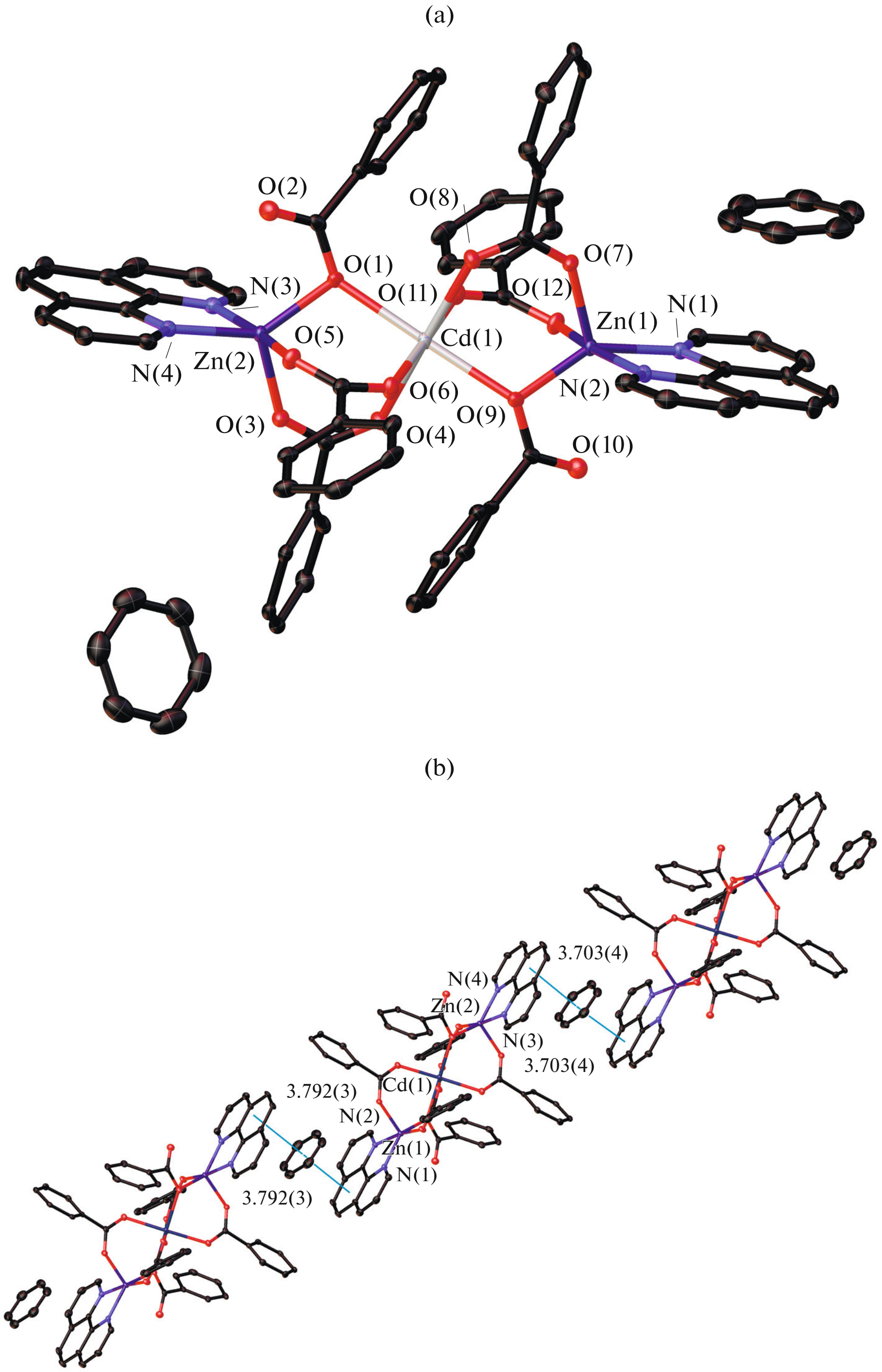


Fig. 5. (a) Structure of complex **IV** and (b) fragment of its crystal packing. Hydrogen and fluorine atoms are omitted.

substantially from all known binuclear cadmium complexes with chelating ligands [17, 26, 31, 54–56]. The arrangement of the aromatic ligands in the $\{Cd_2(Tfbz)_4(Phen)_2\}$ fragment is the same as that in compound **I**. However, the coordination of the water molecule by the Cd atom blocks, most likely, the possibility of forming the 1D structure. In the case of the tetrafluorobenzoate complex, the probability of the appearance of a boundary situation between the formation of the polymer of type **I** and the known binuclear complexes with chelating ligands was confirmed. This result shows that the synthesis of the tetrafluorobenzoate complex with the monodentate aromatic ligand is reasonable. In the binuclear complex with

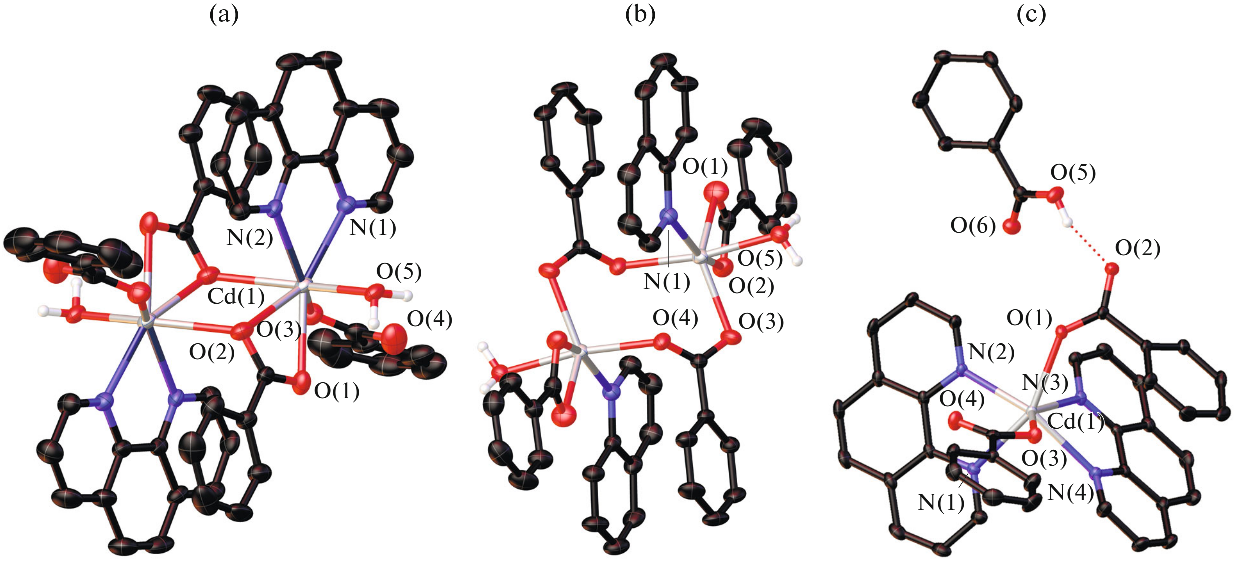


Fig. 6. Structures of complexes (a) **V**, (b) **VI**, and (c) **VII**. Fluorine atoms are omitted. The hydrogen atoms involved in hydrogen bonding are shown.

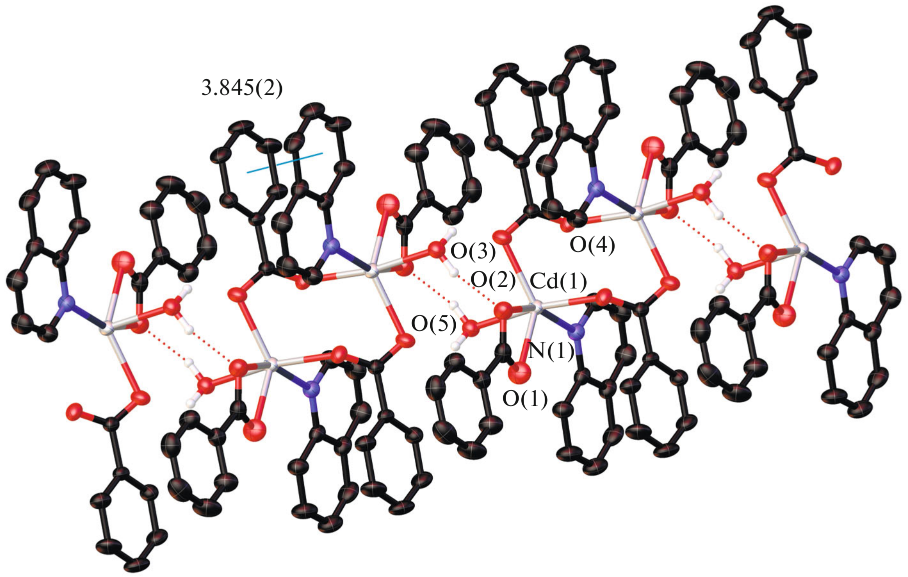


Fig. 7. Fragment of the crystal packing of complex **VI**. Fluorine atoms are omitted. The hydrogen atoms involved in hydrogen bonding are shown.

Quin (**VI**) (Fig. 6b), the geometry of the $\{Cd_2(Tfbz)_4(Phen)_2\}$ fragment was also observed, but the coordination site in the environment of the cadmium atom was occupied by the water molecule, which probably also blocks the possibility of forming the polymeric structure.

Interestingly, the coordination polymer based on the binuclear fragments in which the cadmium atoms bind four bridging carboxyl anions is formed in the case of the pentafluorobenzoate complex with 2,4-lutidine, like that with quinoline being formally α-substituted pyridine [18]. In other words, in the case of the monodentate ligand, we observe the formation (as well as for 1,10-phenanthroline) of a similar binuclear metal carboxylate fragment, which is also stabilized in the form of a molecular compound due to the coordination of water molecules.

In complexes **V** and **VI**, the cadmium atoms are linked to each other by two bridging (complex **VI**) or two chelate-bridging (complex **V**) Tfbz anions. The cadmium atoms in complex **VI** build up their environment to an octahedron by the coordination of the N atom of the Quin molecule, water molecule, and Tfbz anion bound via the chelate mode (CdO_5N). The metal atoms of complex **V** build up their environment to a one-capped trigonal prism (CdO_5N_2) by the coordination of the Phen molecule, water, and oxygen atom of the bridging Pfbz anion coordinated by one O atom. Selected bond lengths and angles for complexes **V** and **VI** are presented in Table 3.

Supramolecular chains along the *a* axis are formed in the packings of complexes **V** and **VI** due to the hydrogen bonding of the coordinated water molecules with oxygen atoms of the Tfbz anions of the adjacent binuclear fragments (Fig. 7).

Each molecule of the N-donor ligand in complexes **V** and **VI** participates in intramolecular stacking interactions with the Tfbz anion and also interacts with the N-donor ligand of the adjacent molecule of the complex. Additional intermolecular stacking interactions are formed between pairs of the Tfbz anions in the packing of complex **VI**, whereas no analogous phenomena are observed in the crystal packing of compound **V**. The fluorine atoms of the carboxylic acid anions are involved in the C–H...F contacts with the hydrogen atoms of the water molecules and N-donor ligands.

The Phen molecules and aromatic fragments of the Pfbz or Tfbz anions in compounds **I** and **V** participate in similar intramolecular stacking interactions. The distance between the Phen and Tfbz planes in complex **V** shortens compared to pentafluorobenzoate polymer **I**, and the Cd...Cd distance in compound **V** elongates. The distances of the C–H...F contacts in complexes **V** and **I** are close.

The shortening of the Cd...Cd distance is observed for complex **V** (4.043(7) Å) compared to that in complex **VI** (4.160(2) Å). The difference in the coordination modes of the Tfbz anions and distances between the metal atoms in compounds **V** and **VI** can be related to stronger intramolecular interactions between the aromatic fragments of the N-donor ligand and carboxylate anions, which is also indicated by the shortening of the distance between the planes of the aromatic ligands (the distances between the centroids and the angle between the planes are 3.846 Å and 8.78° for **VI** and 3.634 Å and 6.57° for **V**). The main angles and distances of intra- and intermolecular interactions for complexes **V** and **VI** are presented in Tables 5 and 6.

The structures of studied compounds **I** and **V** are similar on the whole, in spite of the fact that compound **I** is a polymer and compound **V** is a binuclear complex. The coordination site, which is occupied by the water molecule in compound **V**, in the polymer belongs to the oxygen atom of the carbonyl group of the chelate ligand. The geometry of the binuclear fragments by the possibility of water molecule removing could probably be "ideal" for the self-assembling of a 1D coordination polymer. However, there is one more, perhaps, very significant distinction. All aromatic fragments of the ligands in the polymeric chain are arranged nearly in parallel (the angles between Phen and Tfbz are 9.83° and 11.66°, and those between two Pfbz are 15.19°), whereas in the binuclear complex one of Tfbz is turned nearly perpendicularly to the planes of other ligands (the angles between Phen and Tfbz are 6.31° and 88.87°, and those between two Pfbz are 82.63°). As should be expected, this distinction in the arrangement of the aromatic fragments results in a difference in topology of the $\pi...\pi$ overlaps in the crystal.

As in the case of cadmium pentafluorobenzoate complex **II**, the reaction of cadmium 2,3,4,5-tetrafluorobenzoate with a twofold excess of Phen (Cd : L = 1 : 2) affords mononuclear complex **VII** (Fig. 6c). In the structure of complex **VII**, the cadmium atom builds up its environment to a trigonal prism by the coordination of four N atoms of two Phen molecules and two O atoms of two Tfbz anions (CdO_2N_4). The main distances and angles of complex **VII** are presented in Table 3.

The HTfbz molecule, which is not involved in coordination to the metal atom, is bound via the hydrogen bond to the oxygen atom of the carboxyl group of the Tfbz anion. The coordinated Phen molecules are involved in inter- and intramolecular stacking interactions with the aromatic fragments of the coordinated Tfbz anions. Selected distances and angles of intra- and intermolecular interactions in complex **VII** are presented in Tables 5 and 6.

Thus, we synthesized three compounds (**II**, **IV**, and **VI**) in which one coordinated Phen molecule falls onto one metal atom. Zinc carboxylates, as well as other analogous 3*d*-metal complexes of this composition, are characterized by the mononuclear structure [57–63]; i.e., in the case of zinc pentafluorobenzoates, we failed so far to detect any structure in the crystalline state, which would not be typical of 3*d* metals. This is due, most likely, to shorter bonds formed by these metals. A comparison of complexes **II** and **VI** shows that the structures of the binuclear fragments "cut" from the polymeric chain of compound **II** and complex **VI** are rather close. The coordinated Phen molecules and aromatic fragments of the Pfbz and Tfbz anions are involved in similar intramolecular stacking interactions. However, the coordination polymer is formed in the case of the pentafluorobenzoate compound, whereas the stabilization of the binuclear molecular complex due to the coordination of water molecules is observed for tetrafluorobenzoate. It is poorly probably that cadmium exists as an analogue of complex **VI** in the solution from which the coordination polymer crystallizes, since this complex would be stable as, e.g., aforementioned $[Cd(H_2O)(Pfbz)_2(Bipy)]_n$. Moreover, it seems poorly probable that cadmium exists as binuclear complexes $[Cd_2(Phen)_2(OOCR)_4]$ characteristic of the cadmium trifluorobenzoate, monofluorobenzoate, and benzoate compounds in which the carboxylate anions and chelating ligands shield the metal centers, thus providing the stability of the molecular structure. Our recent data show that the very different types of the pentafluorobenzoate complexes with the coordination of monodentate or chelating ligands are characterized by metal center deblocking due to intramolecular stacking interactions and the formation of coordination polymers [18], whereas the formation of a stable molecular complex needs the coordination of two molecules of the chelating N-donor ligand as it was observed for compound **III**. In this case, it can be assumed that in the solution from which coordination polymer **II** crystallizes cadmium exists as a complex with a different structure compared to the known tetrafluorobenzoate and trifluorobenzoate binuclear compounds. Unlike 3*d* metals, cadmium with chelating ligands can form not only binuclear complexes with two bridging (or chelate-bridging) carboxylate anions but also four-bridge complexes with the Chinese lantern structure [64–66]. It can be assumed that the coordination polymer is formed due to the interaction of the binuclear complexes with the Chinese lantern structure. Our assumption can indirectly be confirmed by the example of forming the coordination polymer of four-bridge fragments $[Cd_2(2,4\text{-}Lut)_4(Pfbz)_4]$ [18]. On the one hand, a nondehydrated commercial solvent and the initial cadmium salt probably were the water sources in the cases of compounds **VI** and **VII**. On the other hand, this solvent was used for the synthesis of compounds **II** and **III**, but the synthesized cadmium complexes contained no water molecules. In the case of water molecule removal, the geometry of the binuclear fragments would be "ideal" for the self-assembling of a 1D coordination polymer. The coordinated water molecule turned out to be very strongly bound: only the starting complex **VI** was isolated after 2-h reflux of a toluene solution of compound **VI**.

Evidently, both intramolecular interactions leading to metal center deblocking and the absence in the reaction medium (in the reaction solution) of molecules stabilizing the reactive metal fragments in the form of stable molecular complexes must be attained in order to form the structure of the coordination polymer by means of the discussed stacking interactions of the fluorinated aromatic fragments and aromatic N-donor ligands.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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