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Influence of the Arene/Perfluoroarene Ratio on the Structure and Non-Covalent Interactions in Crystals of Cd(II), Cd(II)-Tb(III) and Cu(II) Compounds

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Abstract: The influence of arene/perfluoroarene ratio on the structure and crystal packing of carboxylate and nitrate-carboxylate complexes of Cd, Cd-Tb and Cu was studied, using the following compounds: pentafluorobenzoate (pfb) and 4-allyl-2,3,5,6-tetrabenzoate (Afb) anions and 1,10-phenanthroline (phen) composition $[Cd(pfb)_2(phen)]_n$ (**1**), $[Cd(NO_3)(pfb)(phen)]_n$ (**2**), $[Tb_2Cd_2(pfb)_{10}(phen)_2]\cdot 3MeCN]_n$ (**3**), $[Tb_2Cd_2(NO_3)_2(pfb)_8(phen)_2\cdot 1.5MeCN]_n$ (**4**), $[Cu_2(Afb)_4(phen)_2]$ (**5**), $[Cu_2(NO_3)_2(Afb)_2(phen)_2]$ (**6**). It is shown that the main contribution to the stabilization of the crystal packing of coordination polymers **1–4** and molecular binuclear complexes **5** and **6** can be attributed to non-covalent π···π, C-H···F, and C-F···π interactions. It was found that the partial exchange of pfb or Afb anions on compact NO_3^- anions leads to a decrease in steric hindrance, a more efficient overlap of aromatic fragments, and a significant change in the geometry of complexes. Synthesized compounds were characterized by X-ray diffraction analysis, IR spectroscopy, and CHN analysis. The thermal stability of complexes **1** and **2** was studied. Non-covalent interactions were analyzed using the Hirshfeld surface method.

Keywords: complexes of cadmium; terbium and copper(II); pentafluorobenzoates; 4-Allyl-2,3,5,6-tetrafluorobenzoates; directed synthesis; non-covalent interactions; Hirshfeld surface

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Citation: Voronina, J.K.; Yambulatov, D.S.; Chistyakov, A.S.; Bolot'ko, A.E.; Efromeev, L.M.; Shmelev, M.A.; Sidorov, A.A.; Eremenko, I.L. Influence of the Arene/Perfluoroarene Ratio on the Structure and Non-Covalent Interactions in Crystals of Cd(II), Cd(II)-Tb(III) and Cu(II) Compounds. *Crystals* **2023**, *13*, 678. https://doi.org/10.3390/cryst13040678

Academic Editor: Kil Sik Min

Received: 6 March 2023
Revised: 11 April 2023
Accepted: 12 April 2023
Published: 14 April 2023

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1. Introduction

In our work, we draw attention to the known systems of organic compounds that combine perfluorinated and non-fluorinated aromatic fragments ("arene-perfluoroarene") [1–3]. In such systems, dense stack packing of aromatic rings and their convergence to distances of up to 3.4–3.6 Å are often observed due to stacking interactions of the "arene-perfluoroarene" type with the contribution of other types of non-covalent interactions (C-H···F, F···F, etc.). These non-covalent interactions are realized by combining π-saturated and π-deficient aromatic fragments and can be used to obtain a certain structural type [4–7], to stabilize molecules [8] or for their preorganization for [2+2]-cycloaddition [9] and various other problems. The combination of such aromatic fragments with the use of appropriate ligands can significantly expand the possibilities of targeted synthesis of coordination compounds.

One of the most common π-deficient ligands is the anion of pentafluorobenzoic acid. We have previously shown that non-covalent interactions of the π···π type can contribute to the stabilization of coordination polymers at compositions typical for molecular complexes in the case of cadmium complexes with pentafluorobenzoic acid anions and chelating *N*-donor ligands [10–13]. In such structures, the aromatic π-saturated and π-unsaturated fragments that are oriented parallel to each other enter into π···π interactions and form a stacked packing.

The ratio of pentafluorophenyl substituents and π-donor aromatic fragments in polymer structures can be different: $[Cd(H_2O)_4(fur)(pfb)]$, [14] $[Cd(pfb)_2(phen)]_n$, [12] $[Cd(pfb)_3]_n \cdot n(bquinH)$ [11] (pfb—pentafluorobenzoic acid anion; phen—1,10-phenanthroline; bquinH-7,8-benzoquinolinium cation), $[Cd_2Ln_2(pfb)_{10}(phen)_2]_n$ [13]. These compounds have ratios of 1:1, 2:1, 3:1 and 5:1, respectively. However, it can be assumed that the most favorable ratio under appropriate conditions is 1:1, given the composition and structure of the co-crystal of benzene-hexafluorobenzene and other similar systems. With significant deviations from this ratio, the parallel orientation of some of the aromatic fragments is a forced one, and under other conditions, it may be different.

In this paper, we present a study on the effect of replacing the bulky π-acceptor pentafluorobenzoate or 4-allyl-2,3,5,6-tetrafluorobenzoate ligand with a compact π-donor nitrate anion on the structure of Cd(II), Cd(II)-Tb(III), and Cu(II) complexes. The 4-allyl-2,3,5,6-tetrafluorobenzoic acid anion is used because of its potential possibility to undergo [2+2]-photocycloaddition reaction in the solid phase. Non-covalent "arene-fluoroarene" interactions can contribute to the formation of certain mutual orientations required for carrying out reactions of photoinduced [2+2] cycloaddition, which can be used for post-synthetic modification of the obtained complexes [15,16] or to obtain photosensitive materials [17,18].

A significant increase in the number of interactions of the "arene-perfluoroarene" type, as well as the appearance of a number of weaker non-covalent interactions in nitrate-fluorobenzoate complexes, leads to a change in the mutual orientation of aromatic substituents with the formation of a very favorable conformation stabilized by endless stacking interactions and the appearance of dense stable crystals. Information about conditions for the formation of coordination compounds with the strongest pi...pi interactions between aromatic ligands can be useful for the synthesis of complexes of rare-earth elements (REEs) as the extension of the stacking system in a crystal can lead to a significant improvement in the luminescent properties of compounds [19,20], which is necessary to create promising molecular photoluminescent and sensory materials (bulk composites, films, coatings, etc.) [21,22].

2. Experimental

2.1. Materials and Methods

All synthetic work was carried out in air using MeCN (99%, "Chimmed", Moscow, Russia), MeOH (99%, "Chimmed", Moscow, Russia), EtOH (96%, "Ferein", Elektrogorsk, Moscow, Russia), $Cd(NO_3)_2 \cdot 4H_2O$ (99%, "Acros organics", Geel, Belgium), $Tb(NO_3)_3 \cdot 6H_2O$ (99.99%, "Lanhit", Moscow, Russia), $Cu(CH_3COO)_2 \cdot H_2O$ («AR», Russia), $Cu(NO_3)_2 \cdot 6H_2O$ («AR», Russia), pentafluorobenzoic acid (Hpfb, 98%, "P&M-Invest", Moscow, Russia), 4-allyl-2,3,5,6-tetrafluorobenzoic acid (HAfb, 97%, "P&M-Invest", Moscow, Russia), KOH (98+%, «AR», Russia), and 1,10-phenanthroline monohydrate (phen, 99%, "Aldrich-Chemie", Schnelldorf, Germany). Kpfb was synthesized by reacting KOH with Hpfb in ethanol. Elemental analysis was carried out using an EA1108 Carlo Erba automatic CHNS-analyzer (EuroVector, Pavia PV, Italy). IR spectra of the compounds were recorded on a Perkin Elmer Spectrum 65 spectrophotometer (Perkin Elmer, Waltham, MA, USA) equipped with a Quest ATR Accessory (Specac, Orpington BR5 3FQ, UK) by the attenuated total reflectance (ATR) in the range 400–4000 cm^{-1}. Differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) were performed using the differential scanning calorimeter, DSC-60 Plus, and simultaneous thermal analyzer, DTG-60, respectively (Shimadzu, Kyoto, Japan). All experiments were carried out under argon flow at a heating rate of 10 °C/min.

2.2. Synthesis of the Compounds

Synthesis of $[Cd(pfb)_2(phen)]_n$ (**1**).

Pentafluorobenzoic acid (0.137 g, 0.648 mmol) and potassium hydroxide (0.036 g, 0.648 mmol) were dissolved in 25 mL of methanol by stirring. After that, cadmium(II) nitrate tetrahydrate (0.100 g, 0.324 mmol) was added to the mixture, and a white suspension of potassium nitrate was formed immediately. After 15 min of stirring, the mixture was

filtered from KNO_3, and 1,10-phenanthroline monohydrate (0.064 g, 0.324 mmol) was dissolved in the mother liquor by stirring. The colourless solution was allowed to stand at room temperature to slowly evaporate in the air. After 5 days, colourless needle-shaped crystals suitable for X-ray were formed. The yield of compound **1** is 0.145 g (62.5%) based on $Cd(NO_3)_2 \cdot 4H_2O$.

Found, %: C 43.61; H 1.45; N 4.04.

For $C_{26}H_4O_4N_2F_{10}Cd$

Calculated, %: C 43.78; H 1.11; N 3.93.

IR-spectrum (ATR; ν, cm^{-1}): 1910 w, 1723 w, 1685 w, 1671 w, 1699 w, 1645 m, 1592 s [$\nu_{as}(COO^-)$], 1545 m, 1489 s [$_{ar}$(C-C)], 1431 m, 1385 s [$\nu_{sy}(COO^-)$], 1283 w, 1222 w, 1138 m, 1102 m, 990 s [γ_{ar}(C-C)], 930 m, 846 m [$_{ar}$(C-C)], 827 w, 760 s, 727 m [$_{ar}$(C-C)], 696 w, 642 w, 620 w, 582 w, 550 w, 505 w, 461 w, 420 m.

Synthesis of $[Cd(NO_3)(pfb)(phen)]_n$ (**2**).

Pentafluorobenzoic acid (0.137 g, 0.648 mmol) and potassium hydroxide (0.036 g, 0.648 mmol) were dissolved in 15 mL of methanol by stirring. After that, cadmium(II) nitrate tetrahydrate (0.200 g, 0.648 mmol) was added to the mixture, and a white suspension of potassium nitrate was formed immediately. After 30 min of stirring, the mixture was filtered from KNO_3 and 1,10-phenanthroline monohydrate (0.128 g, 0.648 mmol) and was dissolved in the mother liquor upon stirring. The colourless solution was allowed to stand at room temperature to slowly evaporate in the air. After 3 days, colourless needle-shaped crystals suitable for X-ray were formed. The yield of compound **2** is 0.196 g (53.5%) based on $Cd(NO_3)_2 \cdot 4H_2O$.

Found, %: C 40.48; H 1.64; N 7.21.

For $C_{19}H_8O_5N_3F_5Cd$

Calculated, %: C 40.39; H 1.41; N 7.44.

IR-spectrum (ATR; ν, cm^{-1}): 3674 w, 3063 w, 2989 w, 2901 w, 1620 w, 1577 m [$\nu_{as}(COO^-)$], 1511 m, 1497 m [$_{ar}$(C-C)], 1402 s [$\nu_{sy}(COO^-)$], 1296 s, 1224 m, 1140 w, 1102 m, 1035 m, 991 m [γ_{ar}(C-C)], 901 w, 847 s [$_{ar}$(C-C)], 823 m, 767 m, 722 s [$_{ar}$(C-C)], 638 m, 587 w, 549 w, 508 w, 471 w, 443 w, 416 w.

Synthesis of $[Tb_2Cd_2(pfb)_{10}(phen)_2]$. $3MeCN]_n$ (**3**).

An amount of 0.163 g of Kpfb (0.649 mmol) dissolved in 10 mL of EtOH was added to a solution of 0.100 g cadmium(II) nitrate tetrahydrate (0.324 mmol) in a mixture of 15 mL EtOH and 10 mL MeCN. The mixture was stirred for 10 min at 70 °C, and then a white suspension of KNO_3 was filtered off from the mixture. A suspension obtained by the interaction of 0.146 g of $Tb(NO_3)_3 \cdot 6H_2O$ (0.324 mmol) and 0.244 g of Kpfb (0.972 mmol) in 10 mL of EtOH was added to the filtrate. The reaction mixture was stirred for an additional 10 min at 70 °C and filtered from a white precipitate of KNO_3. An amount of 0.063 g of phen·H_2O (0.324 mmol) was added to the filtrate and the mixture was stirred for another 10 min. The colourless solution was allowed to stand at room temperature to slowly evaporate in the air. After 3 days, colourless crystals suitable for X-ray were decanted, washed with cold acetonitrile (t = ~5 °C) and dried in air. The yield of compound **3** is 0.299 g (58.9%) based on $Cd(NO_3)_2 \cdot 4H_2O$.

Found, %: C 38.17; H 1.03; N 3.26.

For $C_{100}H_{25}O_{20}N_7F_{50}Tb_2Cd_2$

Calculated, %: C 38.37; H 0.84; N 3.12.

IR-spectrum (ATR; ν, cm^{-1}): 2981 w, 1723 m, 1651 m, 1613 s, 1520 s [$\nu_{as}(COO^-)$], 1490 s [$_{ar}$(C-C)], 1430 m, 1390 s [$\nu_{sy}(COO^-)$], 1316 m, 1227 m, 1140 w, 1103 s, 989 s [γ_{ar}(C-C)], 929 m, 855 w, 844 s [$_{ar}$(C-C)], 831 m, 761 m, 741 s, 725 s [$_{ar}$(C-C)], 707 s, 642 m, 584 w, 504 w, 459 m, 451 w, 432 w, 419 w.

Synthesis of $[Tb_2Cd_2(NO_3)_2(pfb)_8(phen)_2 \cdot 1.5MeCN]_n$ (**4**).

An amount of 0.163 g of Kpfb (0.649 mmol) dissolved in 10 mL of EtOH was added to a solution of 0.100 g cadmium(II) nitrate tetrahydrate (0.324 mmol) in a mixture of 15 mL EtOH and 10 mL MeCN. The mixture was stirred for 10 min at 70 °C, and then a white suspension of KNO_3 was filtered off from the mixture. An amount of 0.146 g of

$Tb(NO_3)_3 \cdot 6H_2O$ (0.324 mmol) was added to the filtrate and the mixture was stirred for 20 min at 70 °C. After this, 0.063 g of phen·H_2O (0.324 mmol) was added and the mixture was stirred for another 10 min. The colourless solution was allowed to stand at room temperature to slowly evaporate in the air. After 5 days, colourless crystals suitable for X-ray were decanted, washed with cold acetonitrile (t = ~5 °C) and dried in air. The yield of compound **4** is 0.237 g (52.7%) based on $Cd(NO_3)_2 \cdot 4H_2O$.

Found, %: C 36.08; H 1.06; N 3.98.

For $C_{83}H_{20,5}O_{22}N_{7,5}F_{40}Tb_2Cd_2$

Calculated, %: C 35.91; H 0.75; N 3.74.

IR-spectrum (ATR; ν, cm^{-1}): 2977 w, 1723 w, 1698 m, 1649 m, 1613 s, 1520 m [$\nu_{as}(COO^-)$], 1490 s [$_{ar}$(C-C)], 1477 w, 1427 m [$\nu_{sy}(COO^-)$], 1317 m, 1294 s, 1224 w, 1144 m, 1101 s, 1047 s, 989 s [γ_{ar}(C-C)], 932 w, 880 w, 844 m [$_{ar}$(C-C)], 833 m, 763 m, 740 w, 724 s [$_{ar}$(C-C)], 640 w, 627 w, 582 m, 551 w, 472 m, 459 w, 442 w, 425 w.

Synthesis of $[Cu_2(Afb)_4(phen)_2]$ (**5**).

$Cu(CH_3COO)_2 \cdot H_2O$ (0.100 g, 0.500 mmol) was dissolved in 20 mL of EtOH at 50 °C, to give a light-green-coloured solution, to which 4-allyl-2,3,5,6-tetrafluorobenzoic acid (0.234 g, 1.00 mmol) was added. After the addition of the acid, the colour of the mixture became lighter. The reaction mixture was stirred for 1 h. After cooling to room temperature, 1,10-phenanthroline monohydrate (0.099 g, 0.500 mmol) was added and the mixture was stirred until the N-donor ligand was fully dissolved. The mixture was allowed to stand at room temperature to slowly evaporate in the air. After 1 month, blue prismatic crystals suitable for X-ray were formed. The yield of compound **5** is 0.301 g (71.9%) based on $Cu(CH_3COO)_2 \cdot H_2O$.

Found, %: C 54.35; H 2.49; N 4.20.

For $C_{64}H_{36}Cu_2O_8N_4F_{16}$

Calculated, %: C 54.13; H 2.61; N 4.05.

IR-spectrum (ATR; ν, cm^{-1}): 3653 w, 3540 w, 3456 w, 3363 w, 3226 w, 3092 w, 2978 w, 2901 w. br, 2356 w, 2279 w, 1582 s [$\nu_{as}(COO^-)$], 1523 m, 1469 s [$_{ar}$(C-C)], 1432 m, 1362 s [$\nu_{sy}(COO^-)$], 1260 m, 1220 w, 1146 w, 1126 w, 1102 w, 1054 w, 1037 w, 979 s [γ_{ar}(C-C)], 909 m [δ(C=C)], 873 m, 848 m [$_{ar}$(C-C)], 798 m, 742 s, 721 s [$_{ar}$(C-C)], 653 m, 523 m, 507 m, 477 m, 425 m, 411 m.

Synthesis of $[Cu_2(NO_3)_2(Afb)_2(phen)_2]$ (**6**).

KOH (0.046 g, 0.82 mmol) and 4-allyl-2,3,5,6-tetrafluorobenzoic acid (0.194 g, 0.820 mmol) were dissolved in 20 mL EtOH. The reaction mixture was heated at 50 °C, and 0.100 g of $Cu(NO_3)_2 \cdot 3H_2O$ (0.410 mmol) was added next. A change in the colour of the mixture from light yellow to light green with a subsequent white suspension of KNO_3 was observed. After one hour of stirring, heating was stopped, and the mixture was cooled to room temperature and filtered from the white precipitate. 1,10-phenanthroline monohydrate (0.082 g, 0.410 mmol) was added to the filtrate, and the mixture was stirred until the full ligand dissolved. The mixture was allowed to stand at room temperature to slowly evaporate in the air. After 3 weeks, blue prismatic crystals suitable for X-ray were formed. The yield of compound **6** is 0.165 g (56.1%) based on $Cu(NO_3)_2 \cdot 3H_2O$.

Found, %: C 54.37; H 2.40; N 4.21.

For $C_{64}H_{36}Cu_2O_8N_4F_{16}$

Calculated, %: C 54.16; H 2.68; N 4.01.

IR-spectrum (ATR; ν, cm^{-1}): 3652 w, 3540 w, 3456 w, 3356 w, 3236 w, 3091 w, 2867 w. br, 2285 w, 2002 w, 1691 w, 1679 m, 1671 m, 1564 s [$\nu_{as}(COO^-)$], 1519 m, 1467 s [$_{ar}$(C-C)], 1431 m, 1361 s [$\nu_{sy}(COO^-)$], 1260 m, 1208 m, 1146 w, 1127 w, 1102 w, 1053 w, 1034 w, 978 m [γ_{ar}(C-C)], 908 m [δ(C=C)], 873 m, 848 m [$_{ar}$(C-C)], 798 m, 741 s, 721 s [$_{ar}$(C-C)], 653 m, 520 m, 507 m, 474 m, 420 m.

2.3. X-ray Diffraction Studies

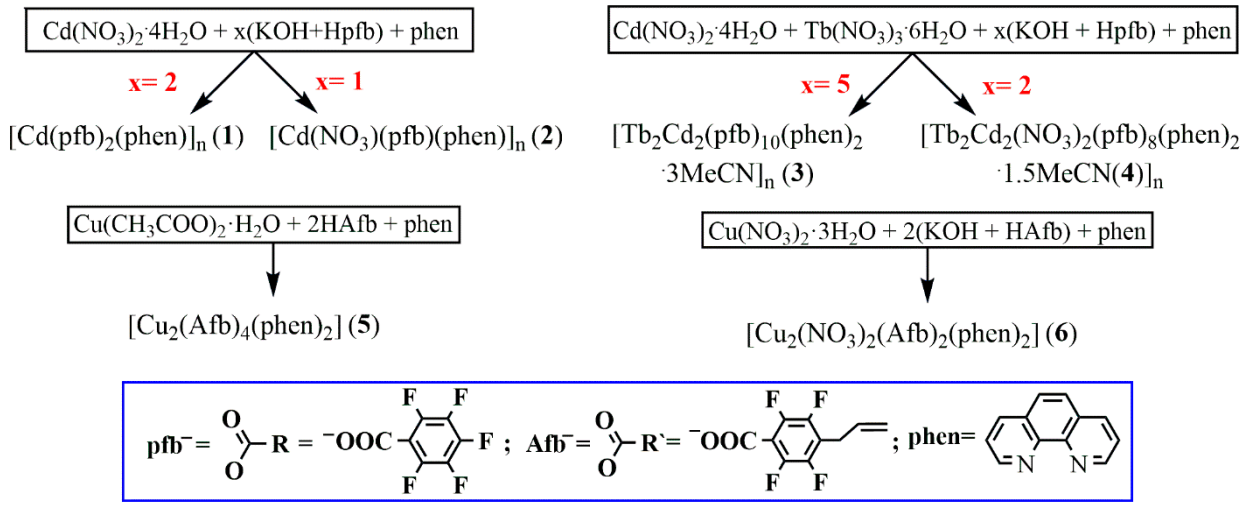
Single-crystal X-ray diffraction experiments were performed using a Bruker Apex II diffractometer with a CCD camera and a graphite monochromated MoK radiation source

(MoKα, λ = 0.71073 Å). Semiempirical absorption corrections were applied for all the experiments using SADABS (University of Gottingen, Gottingen, Germany) [23]. The structure was solved by the direct method and refined using the least squares method; first, in the isotropic and then in the anisotropic approximation in terms of F^2_{hkl} [24]. The H atoms were calculated geometrically and refined using the riding model. The calculations were performed in SHELXL-2018/3 [25] using Olex2 (OlexSys Ltd., Chemistry Department, Durham University, Durham DH1 3LE, UK) [26]. SHAPE 2.1 software (University of Barcelona, Barcelona, Catalonia, Spain) [27] was used to determine the geometry of metal polyhedrals. For structure **6,** the contribution of disordered solvent molecules was treated as a diffuse using a Squeeze procedure implemented in the Olex2 program [28]. The crystallographic parameters and details of the refinement for **2**, **4**, **5**, and **6** are reported in Table S1. Structural data of compounds **2**, **4**, **5**, and **6** can be obtained from The Cambridge Crystallographic Data Centre (CCDC № 2,237,100 (2), 2,237,102 (4), 2,237,101 (5), 2,237,103 (6) via deposit@ccdc.cam.ac.uk). The Hirshfeld surface was analyzed using the Crystal Explorer 17 program to evaluate the contribution of various non-covalent interactions to the crystal packings of the resulting complexes [29,30].

3. Results

3.1. Synthesis of Complexes

By varying the ratio of reagents in the reactions of metal nitrates with the potassium salt of pentafluorobenzoic acid and 1,10-phenanthroline (Scheme S1), the previously described pentafluorobenzoate homometallic $[Cd(pfb)_2(phen)]_n$ (**1**) [12] and heterometallic $[Tb_2Cd_2(pfb)_{10}(phen)_2{\cdot}3MeCN]_n$ (**3**) [13] and new nitrate-pentafluorobenzoate homo- $[Cd(NO_3)(pfb)(phen)]_n$ (**2**) and heterometallic $[Tb_2Cd_2(NO_3)_2(pfb)_8(phen)_2{\cdot}1.5MeCN]_n$ (**4**) coordination polymers were obtained.



Scheme 1. Synthesis of complexes **1**–**6**.

The reaction of 2,3,5,6-tetrafluoro-4-allylbenzoate with various copper salts and 1,10-phenanthroline was also studied. Thus, using copper nitrate, the compound $[Cu_2(NO_3)_2(Afb)_2(phen)_2]$ (**6**) was obtained, whereas complex $[Cu_2(Afb)_4(phen)_2]$ (**5**) was obtained using only copper acetate as the initial salt.

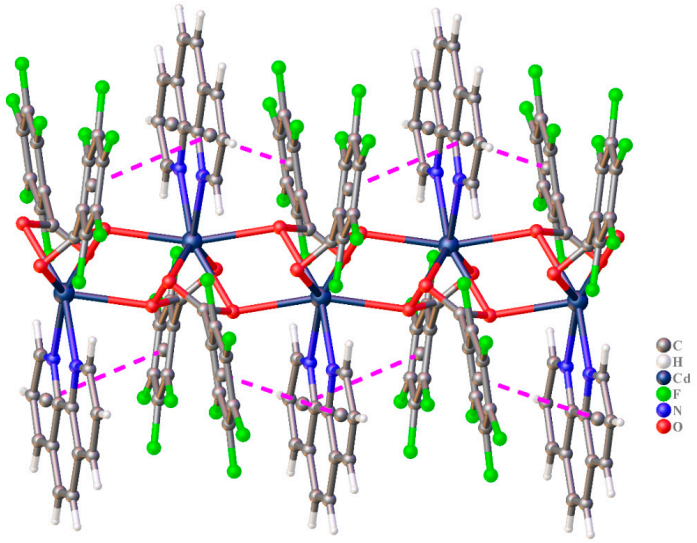
The IR spectra of the obtained compounds show the presence of acid anions—pentafluorobenzoic acid for coordination polymers **1**–**4** (Figures S1 and S2 see Supplementary Materials) and 4-allyl-2,3,5,6-tetrafluorobenzoic acid for molecular complexes **5** and **6** (Figure S3), which are confirmed by strong symmetric and asymmetric stretching vibrations of carboxyl groups in the range of 1595–1385 cm^{-1} for **1**–**4** and 1582–1361 cm^{-1} for **5** and **6**, respectively, and skeletal vibrations of the aromatic ring of acid in the range of 999–978 cm^{-1} for **1**–**6**. Strong vibrations of pentafluoroarene fragments in **1**–**4** and tetraflu-

oroarene fragments in **5** and **6** are located at a range of 1497–1469 cm^{-1}. Characteristic bands of medium and strong intensity in the region of 848–844 cm^{-1} and 727–721 cm^{-1} indicate the presence of phenanthroline with its conjugated aromatic structure. For **5** and **6**, we observed bands from the bending vibration of allyl fragments at 909 and 908 cm^{-1}, respectively. For compounds **4** and **6,** vibrational bands were observed in the region of 1698 cm^{-1}, and 1679 cm^{-1}, respectively, which belong to structural vibrations of nitrate anions present in the structures. For compound **2**, vibrational symmetrical bands of nitrates can be observed at 1224 cm^{-1}.

3.2. The Structure of Complexes

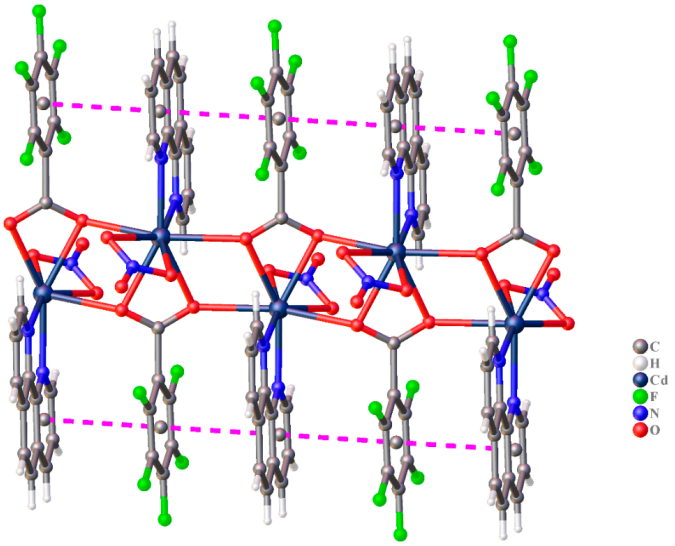
3.2.1. The Structure of Complexes **1** and **2**

The formation of the polymer chain of complexes **1** (Figure 1a) and **2** (Figure 1b) occurs due to the chelate-bridge coordination of pentafluorobenzoate fragments (μ^2κO:κ^{2}O,O′ for **1** and μ^2κO:μ^2κO′ for **2**) that bind cadmium ions. The coordination polyhedron of metal ions in both complexes is a slightly distorted square antiprism (CShM = 3.194 in **1** and 2.991 in **2**) formed by a phen molecule and four pfb fragments in **1** and by a phen molecule, three pfb fragments, and one κ^{2}O,O′ nitrate anion in **2**. In both complexes, metal ions lie in the same plane relative to which it is convenient to analyze the geometry of molecules. Thus, in compound **1**, the coordination of bulky ligands on each cadmium ion results in the fact that they are located as uniformly as possible relative to the plane in which the metal atoms lie. The plane of the phenanthroline fragment is rotated relative to the plane of metals by 58.05(2)° and to the planes of pentafluorobenzene rings—by 64.76(6)° and 64.63(4)°, although their arrangement relative to each other is close to parallel (angles C_6F_5-Phen are 10.21(4) and 9.80(5)°). With such an arrangement, one would expect the presence of π···π interactions; however, because repulsive forces act between pentafluorobenzene rings, leading to a maximum shift in aromatic fragments relative to each other, the molecule has a geometry in which all rings are arranged in a spiral and overlap each other minimally. The result of this is that only a small edge π···π overlap of phenanthroline—pentafluorobenzoate occurs (Table S2). Thus, in a crystal, infinite polymer chains directed along the 0c axis are linked to each other by C-H···O and C-H···F interactions (Table S3) with the formation of a supramolecular layered structure. In this case, it is possible to suggest that the stacking interactions of the "arene-perfluoroarene" type are the driving force of the formation of the polymer structure, but the stabilization of the crystal structure is largely or even mainly associated with other types of non-covalent interactions.



(**a**)

Figure 1. *Cont.*



(**b**)

Figure 1. Structure of chains of polymer compounds **1** (**a**) and **2** (**b**) in crystals.

The dotted line shows π··· π interactions.

When one pentafluorobenzoate anion is replaced by a more compact nitrate anion in the case of complex **2**, the structure of the polymer chain changes rather significantly. A decrease in the symmetry of the complex leads to the fact that the Cd-O-Cd bridging fragments become asymmetric and the Cd-Cd distances in the complexes differ (4.0083(3) Å in **1** and 4.007(1) Å and 4.100(1) Å in **2**). The range of Cd-O distances in the four-membered bridge fragment also expands slightly (Table 1). Two bridging oxygen atoms lie in the plane formed by cadmium ions, but the other two deviate from it by about 34°. The planes of all aromatic fragments of the ligands are located almost perpendicular to the metal plane: the angle with the phenanthroline fragment is 92.5(1)°, with the pentafluorobenzene ring—83.6(2)°, and with the nitro group—84.4(2)°. The alternating phenanthroline and pentafluorobenzoate fragments, which are opposite each other, are practically parallel to each other (angle 4.6(2)°). In this case, the nitro group is rotated by 58.5(2)° with respect to the phenanthroline and by 55.9(3)° with respect to the pentafluorobenzene cycles. This arrangement is apparently stabilized by three short contacts involving the O1 atom: with carboxylate oxygens of two different pentafluorobenzoates and LP···π with the phenanthroline fragment. In all cases, the distances between the corresponding atoms are shorter than the sum of the van der Waals radii. All these contacts are insignificant but comparable energies, and their different directions lead to an unusual arrangement of the nitrate ligand. However, such an arrangement and a small volume of this ligand contribute to the most favorable arrangement of aromatic fragments, as a result of which the polymer chain is quite compact, the bulky ligands strictly overlap each other and are located symmetrically above and below the main plane of the molecule. Such a mutual arrangement of fragments with electron-donating and electron-withdrawing substituents leads to very strong π···π interactions (Table S2), as a result of which endless stacks of alternating pentafluorophenyl substituents of the carboxylate anion and coordinated molecules of 1,10-phenanthroline are formed on both sides of the main plane of the polymer. The polymer chains are located along the crystallographic 0a axis and are linked into a three-dimensional supramolecular network by weak C-H···O and C-H···F interactions (Table S3). It is interesting that, in contrast to the molecules of compound **1**, in which the ligands are evenly distributed around the metal core, in complex **2,** their arrangement is more compact, as a result of which the volume of the molecule is much smaller (Figure S4); whereas, the packing factor (72.0 for compound **1** and 74.2 for compound **2**) and the density (1.995 g/cm^3 and 2.08 g/cm^3 in **1** and **2**, respectively) are slightly higher.

Table 1. Main bond lengths for complexes **1–6**.

Bond	*d*/Å					
	1 **M = Cd**	**2** **M = Cd**	**3** **M = Cd**	**4** **M = Cd**	**5** **M = Cu**	**6** **M = Cu**
M-O (RCOO)	2.425(1)–2.472(1)	2.443(6)–2.510(6)	2.215(4)–2.469(5)	2.279(3)–2.535(4)	1.930(4)–2.380(3)	1.966(2), 2.366(2)
Tb-O (RCOO)	-	-	2.350(3)–2.729(4)	2.335(3)–2.576(3)	-	-
M-N (phen)	2.366(1)	2.313(7), 2.338(7)	2.319(5), 2.324(6)	2.274(4), 2.313(4)	2.024(4), 2.032(4)	1.997(3), 2.003
M-O (NO_3)	-	2.324(7), 2.563(6)	-	-	-	1.970(2)
Tb-O (NO_3)	-	-	-	2.418(3), 2.445(3)	-	-
Tb···Tb	-	-	4.160(2)	4.016(1)	-	-
M···M	4.001(1)	4.007(1), 4.099(1)	3.926(1)	3.730(1)	3.435(1)	3.364(1)

Analysis of the Hirshfeld surface of complex **1** revealed that the largest contribution to the total Hirshfeld surface area was made by C···C, C···F, H···F, F···F, C···H interactions (Table 2, Figure 2, Figure 3, Figure S7 and Figure S8). The replacement of one pentafluorobenzoate anion by the nitrate anion in the case of complex **2** leads to a significant increase in the contribution of C···C, F···F, O···H interactions and to a decrease in the contributions of H···F and C···H interactions.

Table 2. Contribution of non-covalent interactions to the total Hirshfeld surface of complexes **1–6**.

Interaction	Compound					
	1	**2**	**3**	**4**	**5**	**6**
C···C	5.6%	11.2%	3.8%	1.8%	4.1%	5.6%
C···F	15.8%	13.8%	13.8%	14.9%	3.2%	4.6%
H···F	29.0%	25.7%	23.3%	17.4%	36.4%	23.4%
F···F	17.0%	28.8%	28.8%	27.6%	3.3%	0.9%
C···H	11.2%	3.8%	4.7%	9.5%	13.2%	11.2%
O···H	4.0%	14.3%	3.9%	8.4%	12.3%	23.6%

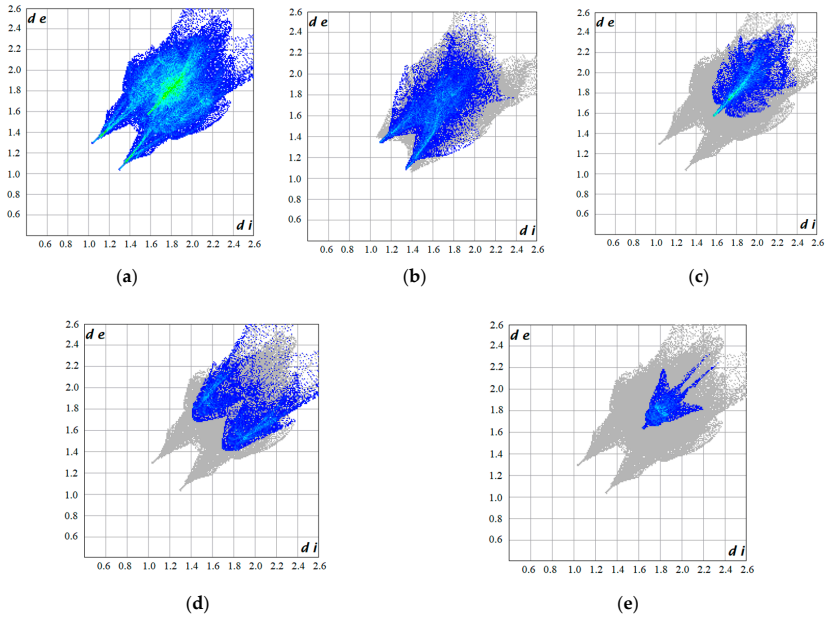


Figure 2. 2D fingerprint plots (**a**) and sections of the graph, which correspond to H···F (**b**), F···F (**c**), C··· F (**d**) and C···C (**e**) interactions in the structure **1**.

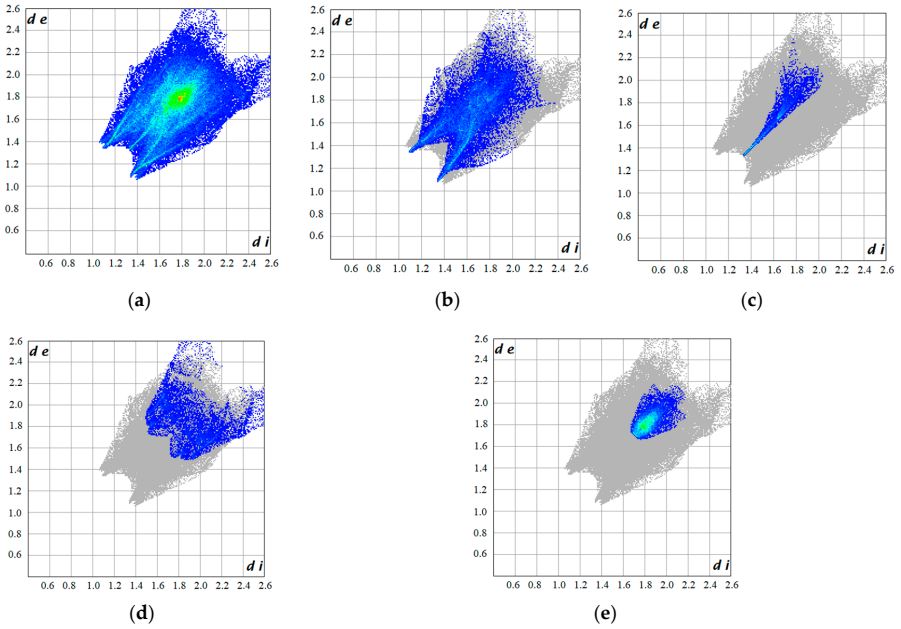


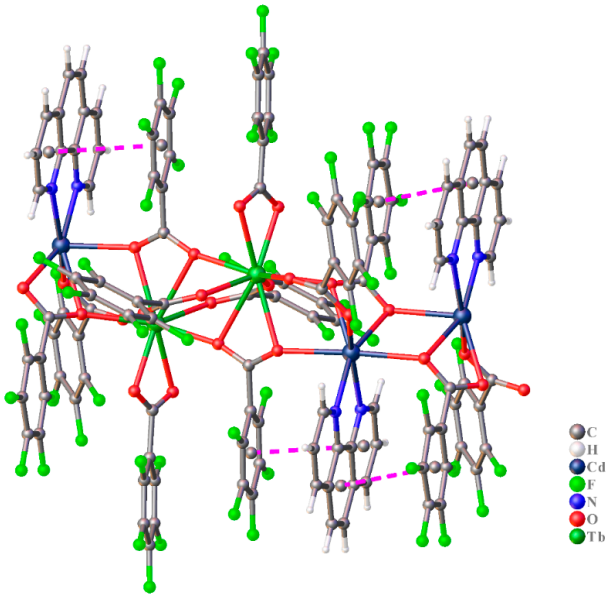
Figure 3. 2D fingerprint plots (**a**) and sections of the graph, which correspond to H···F (**b**), F···F (**c**), C··· F (**d**) and C···C (**e**) interactions in structure **2**.

Thus, the replacement of half of the larger pentafluorobenzoate anions by compact nitrate ones created conditions for the most favorable arrangement of aromatic fragments. As a result of this, a structure was obtained in which pentafluorophenyl substituents of carboxylate anions and coordinated 1,10 phenanthroline molecules alternate and enter into strong stacking interactions.

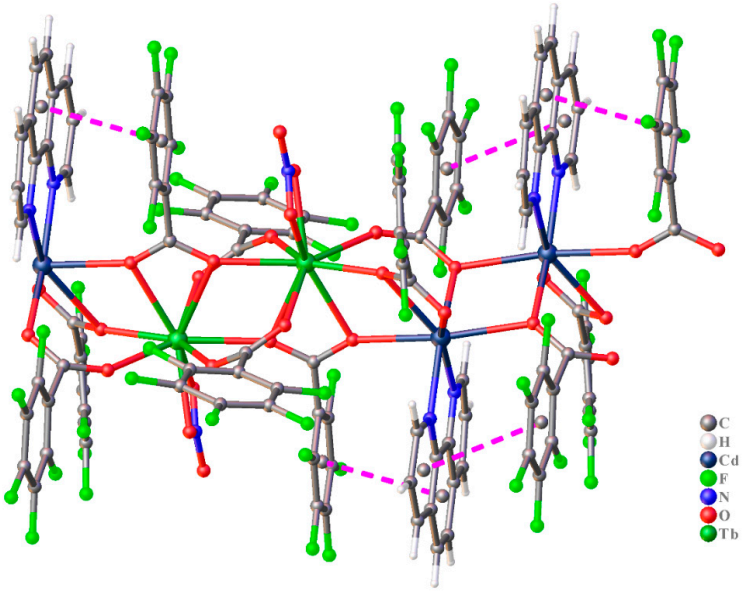
3.2.2. The Structure of Complexes **3** and **4**

A somewhat different result of replacing the pentafluorobenzoate anion with a more compact nitrate anion can be observed upon passing from the heterometallic coordination polymer $[Tb_2Cd_2(pfb)_{10}(phen)_2 \cdot 3MeCN]_n$ (**3**, Figure 4a) to $[Tb_2Cd_2(NO_3)_2(pfb)_8(phen)_2 \cdot 1.5MeCN]_n$ (**4**, Figure 4b). The polymer chain of compounds **3** and **4** is constructed from symmetrical four-nuclear chain puzzle fragments, in which cadmium atoms are peripheral and lanthanide atoms are central, as in molecular complexes of a similar composition. The cadmium atoms of two neighboring fragments are linked by μ^2κO:κ^{2}O,O′ pentafluorobenzoate anions and form a binuclear linking fragment similar in structure to the binuclear fragment of the chain of homometallic compound **1**. It is interesting to analyze the effect of replacing a bulkier pentafluorobenzoate ligand with a small nitrate in heterometallic Cd_2Ln_2 complexes $[Tb_2Cd_2(pfb)_{10}(phen)_2 \cdot 3MeCN]_n$ (**3**, Figure 4a) and $[Tb_2Cd_2(NO_3)_2(pfb)_8(phen)_2 \cdot 1.5MeCN]_n$ (**4**, Figure 4b). The dicadmium fragments in them are similar in composition and structure to the main fragment of compound **1** and are the connecting link between two tetranuclear monomeric fragments of the polymer. Apparently, due to this, a slight contraction of the four-membered bridge fragments occurs, as a result of which the Cd-Cd distance decreases to 3.926(1) Å in **3** and 3.730(1) Å in **4** (in **1** this distance is slightly longer than 4 Å), the Cd-O distances decrease by an average of 0.2 Å, and the Cd-O-Cd angles decrease from about 108° to 104°. The polyhedron of cadmium ions in both heterometallic complexes represents a one-capped trigonal prism (CShM = 2.015 for **3** and 2.223 for **4**) formed by a phenanthroline molecule and four pentafluorobenzoate anions. Cadmium ions are bound to terbium ions by μ^2κO:κ^{2}O,O′, μ^2κO:μ^2κO′ and μ^2κO:κ^{2}O,O′ pentafluorobenzoate anions. It is interesting to note that the replacement of the pentafluorobenzoate anion in the heterometallic complex occurs not on the cadmium ion, similarly to complex **2**, but on the terbium ion. The central fragment of the tetranuclear monomer of the heterometallic complex consists of two nine-coordinated terbium ions, the polyhedra of

which are formed by six pentafluorobenzoates, one of which is chelate-coordinated, and completed to the muffin polyhedron by two oxygen atoms of the κ^2O,O′ pentafluorobenzoate in **3** and a nitrate anion in **4** (CShM = 1.621 in **3** and 1.617 in **4**). Replacing the bulky pentafluorobenzoate anion with a more compact nitrate anion leads to a decrease in the repulsion effects between ligands and to the contraction of the central fragment, which is reflected in a decrease in the Tb-O and Tb-Tb distance in complex **4** compared to complex **3** (Table 1); however, the Cd-Tb distance slightly increases (3.774(4) in **3** and 3.994(2) Å in **4**). It should be noted that in heterometallic complexes, metal atoms of various types form separate planes, as a result of which it is quite difficult to single out one plane relative to which one can ascribe the structure of the molecule, so the structure is considered relative to the metal core.



(**a**)



(**b**)

Figure 4. Structure of chains of polymer compounds **3** (**a**) and **4** (**b**) in crystals. The dotted line shows π⋯ π interactions. Solvate molecules are not shown.

Some change in the geometry of the cross-linking cadmium bridge in compound **3** compared to compound **1** is reflected in small changes in the arrangement of the aromatic rings of the ligands. The phenanthroline and pentafluorobenzoate rings are practically parallel to each other (the phenanthroline—pentafluorophenyl angles are 2.6(3)° and 2.6(2)°), as in **1**, but such a significant mutual displacement of the centroids of these fragments, as in **1**, is not observed in **3**. Apparently, this is due to the fact that in contrast to **1**, the dicadmium fragments in **3** are isolated from each other, and the same alternation of coordinated molecules of 1,10-phenenthroline and pentafluorophenyl substituents is not observed in the chain of the coordination polymer. The effect of additional cycles of pentafluorobenzoate ligands coordinated on terbium atoms should also be noted. On each side of the nonplanar zigzag chain of metal atoms, two identical stacks of aromatic fragments are formed. As a result, coordinated phenanthroline molecules enter into π···π interaction with the cycle of μ^2κO:κ^{2}O,O′ pentafluorobenzoate coordinated between two cadmium atoms (Table S2). A continuation of the stack of aromatic fragments are aromatic fragments of two pentafluorobenzoate anions that bind lanthanide atoms, forming one phenanthroline-pentafluorophenyl and one pentafluorophenyl-pentafluorophenyl contact.

Two more symmetrically independent pentafluorobenzoate ligands are located parallel to the metal core and are rotated relative to phenanthroline by 11.2(3)° and 79.7(3)°, respectively, hence they are far from each other and do not form intramolecular interactions, being bound by weak van der Waals bonds with solvate molecules of acetonitrile and by the same pentafluorobenzoates of the adjacent polymer chain, forming a three-dimensional crystalline system.

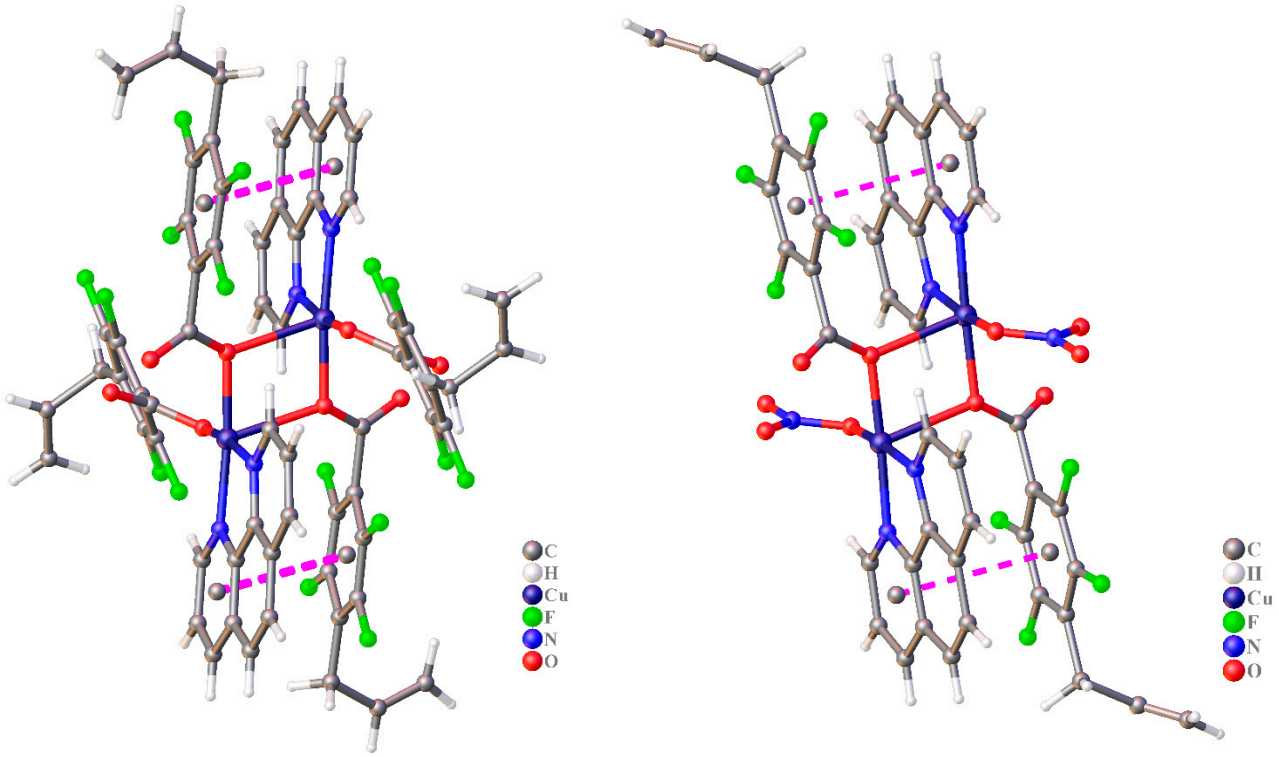
As mentioned above, the replacement of pentafluorobenzoate by nitrate in the homometallic cadmium complex leads to a spatial redistribution of aromatic ligands with the realization of the maximum number of overlaps of arene and perfluoroarene fragments. However, in the case of heterometallic complex **3**, a similar change in the structure of the polymer chain is impossible due to the large preponderance of the number of pentafluorophenyl fragments over the number of coordinated phenanthroline molecules. When comparing the relative arrangement of aromatic ligands and intramolecular non-covalent interactions in compounds **3** and **4**, an interesting feature is observed. Thus, the dicadmium fragment has a structure very similar to that described for compound **1**, in which the phenanthroline fragment is located between two pentafluorophenyl rings, but in this case, one of the pentafluorophenyl rings overlaps quite significantly with the phenanthroline molecule. At the same time, inside the four-nuclear monomeric fragment, planar π-systems, one of which is the nitro group, are located strictly parallel to each other at a minimal distance. Thus, an infinite π-stack is formed on both sides of the polymer chain, in which there are regions of slightly stronger and slightly weaker interactions. In this case, the substituents of two pentafluorobenzoate anions that bind lanthanide atoms, just as in polymer **3**, do not participate in the formation of π···π interactions (Figures 4 and S5).

It was found that the greatest contribution to the Hirshfeld surface of complex **3** is made by C···F, H···F, F···F interactions (Table 2). In the case of the nitrate-pentafluorobenzoate complex **4**, an increase in the contribution of C···H, C···C, and O···H interactions, as well as a decrease in the contribution of H···F interactions is observed (Figures S9–S12).

3.2.3. The Structure of Complexes **5** and **6**

In the case of copper complexes with 2,3,5,6-tetrafluoro-4-allylbenzoic acid anions, we obtained molecular complex $[Cu_2(Afb)_4(phen)_2]$ (**5**, Figure 5a) which was revealed to be a structural analogue of the known copper pentafluorobenzoate complex $[Cu_2(pfb)_4(phen)_2]$ [31]. This one, like complex 5, is interesting in that it has almost the same structure as the binuclear fragment "cut out" from the chain of the coordination polymer $[Cd(pfb)_2(phen)]_n$ **1**. The existence of a molecule with such a geometry is possible due to the tetragonal-pyramidal environment of copper atoms, whereas the copper atoms are coordinatively saturated, although they "look" accessible for additional coordination of ligands. The structure of complexes with 2,3,5,6-tetrafluoro-4-allylbenzoic acid anions is also interest-

ing from the point of view of evaluating the prospects for using compounds in which arene-perfluoroarene stacking is realized, for the preorganization of unsaturated fragments and attempts at subsequent implementation of photochemical 2+2 cycloaddition reactions. By analogy with the synthesis of compound **2**, the nitrate–carboxylate complex $[Cu_2(NO_3)_2(Afb)_2(phen)_2]$ was also obtained (**6**, Figure 5b). This made it possible to state that the observations and conclusions drawn from the analysis of the structure of coordination polymers **1** and **2** are also valid for molecular complexes **5** and **6**, in which the same non-covalent interactions are realized.



(**a**) (**b**)

Figure 5. Molecular structure of **5** (**a**) and **6** (**b**) in crystals. The dotted line shows π···π interactions.

The binuclear complexes **5** and **6** are structurally similar to the binuclear fragments "cut out" from the chain of polymers **1** and **2**, respectively. Cu-Cu distances are 3.435(2) Å and 3.3642(9) Å, Cu–O bonds are in the range of 1.97–2.37 Å and 1.93–2.38 Å in complexes **5** and **6**, respectively, and the Cu–N bonds in both complexes are about 2 Å long. The tetragonal-pyramidal environment of each copper atom (CShM = 2.073(**5**), 2.687(**6**)) in complex **5** is formed by two nitrogen atoms of the chelate-coordinated 1,10-phenanthroline molecule, two common oxygen atoms of μ^2κO-Afb anions, and by an intrinsic oxygen atom of the κO monodentate-coordinated Afb anion. In complex **6,** the place of the monodentately coordinated carboxylate anion is occupied by the monodentately coordinated nitrate anion. The arrangement of the π-systems of ligands in the structure of **5** is such that an intramolecular π···π interaction occurs between phenanthroline and the aromatic fragment of one of the tetrafluoro-4-allyl benzoate anions with a distance between the planes of the interacting fragments of 3.4083(12) Å (Figure 6). The aromatic fragment of the second anion is spatially deployed with respect to the other two ligands, as in the above-described cadmium coordination polymer, as a result of which it does not enter into π···π interactions, forming C-H···π and C-F···π contacts (Figure S6, Tables S2 and S3). With such a structure of the complex, the second side of phenanthroline remains free of intramolecular interactions, resulting in an intermolecular stacking interaction with a distance between the planes of phenanthroline fragments of neighboring molecules of 3.451(2) Å.

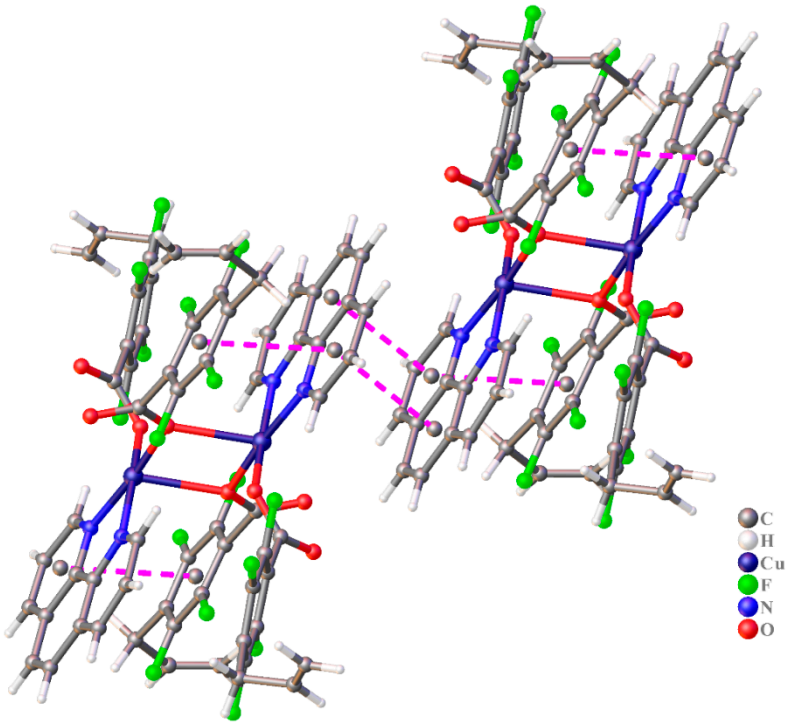


Figure 6. Intra- and intermolecular π···π interactions in a crystal of compound **5**.

Nitrate-carboxylate complex **6** has a similar structure; however, it exhibits greater overlap and a significant reduction in the distances between the planes of aromatic fragments of organic ligands compared to the carboxylate complex (3.295(2) Å), which suggests that the π···π interaction in this case is much higher in energy (Table S3). In this case, the nitrate anions are turned almost perpendicular to the rest of the ligands (the angle with the phenanthroline plane is 80.83(1)°). Such an arrangement of nitrate does not lead to its participation in intramolecular interactions; however, when analyzing the crystal packing, it was found that, in addition to π···π interactions between phenanthroline fragments, two more types of intermolecular interactions involving nitrate anions are realized in this crystal. The first one can be described as a π···π-interaction of delocalized systems of nitrates with a distance between the planes of 2.968(4) Å, and with a distance between nitrogen atoms, which are at the same time centroids of the π-system, −3.446(4) Å. Another interaction of the nitrate anion with the phenanthroline ring, the LP···π interaction, can be described as weak. In this interaction, the oxygen atom of the nitro group acts as a lone electron pair donor (distance between the oxygen atom and: plane of the cycle is 3.020(3) Å). In this case, this interaction competes with the π···π interaction between the phenanthroline fragments, shifting the cycles relative to each other. It should be noted that the distance between the planes is preserved in this case.

When analyzing the Hirshfeld surface of complex **5**, it was revealed that the largest contribution to the total Hirshfeld surface area is made by H···F, O···H, C···H interactions (Table 2). The introduction of the nitrate anion into the coordination environment of the copper ion in the structure of complex **6** leads to an increase in the contribution of C···C and O···H interactions (Figures S13–S16).

3.3. Thermal Decomposition

For two compounds $[Cd(pfb)_2(phen)]_n$ (**1**) and $[Cd(NO_3)(pfb)(phen)]_n$ (**2**) thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) curves were obtained in the temperature range of 25–500 °C under argon flow at a heating rate of 10 °C/min for evaluation of their thermal behavior.

According to TGA, the decomposition of the compounds started at 115 °C and 198 °C for $[Cd(pfb)_2(phen)]_n$ (**1**) and $[Cd(NO_3)(pfb)(phen)]_n$ (**2**), respectively (Figures 7 and 8). Compound **1** slowly loses weight towards the end of heating; however, at 215 °C, a slight jump in mass loss is observed. It corresponds to an exothermic DCS process with a temperature increase up to 217 °C in the heater. For compound **2**, a three-step process of weight loss is observed at a heat range of 198–226 °C and one complex two-step process at a heat range from 230–402 °C followed by a plateau. According to DSC data, compound **1** shows one complex endothermic process that can be observed at a range between 154 °C to 198 °C with a peak of 179 °C and an exothermic process at a range of 208–216 °C with a peak at 215 °C. For compound **2**, three processes are observed: one endothermic at range 221–232 °C, and two exothermic at 253–269 °C and 360–372 °C, which correspond to the processes of weight change.

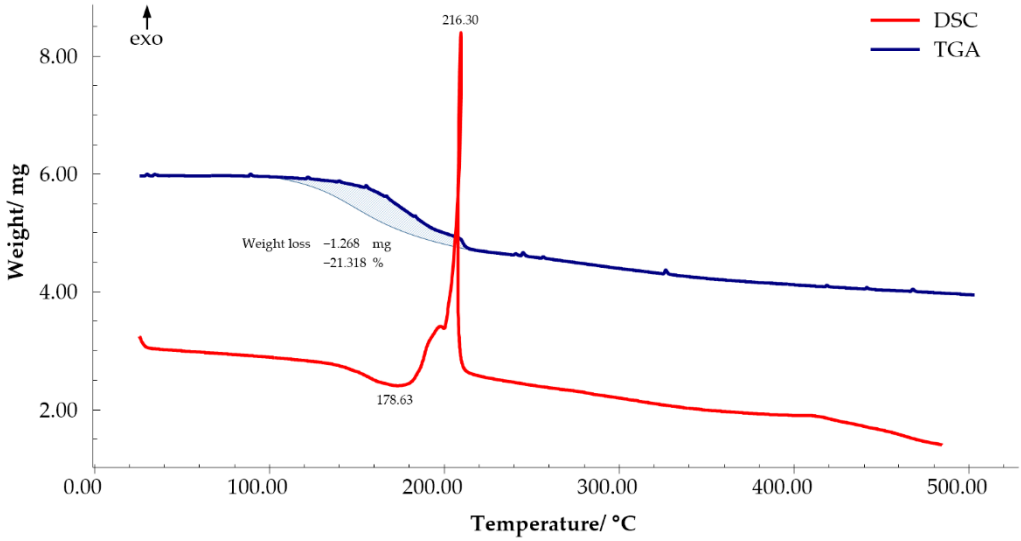


Figure 7. Thermal analyses (thermogravimetry with insert of differential scanning calorimetry) of $[Cd(pfb)_2(phen)]_n$ (**1**). Blue—TGA curve, Red—DSC curve.

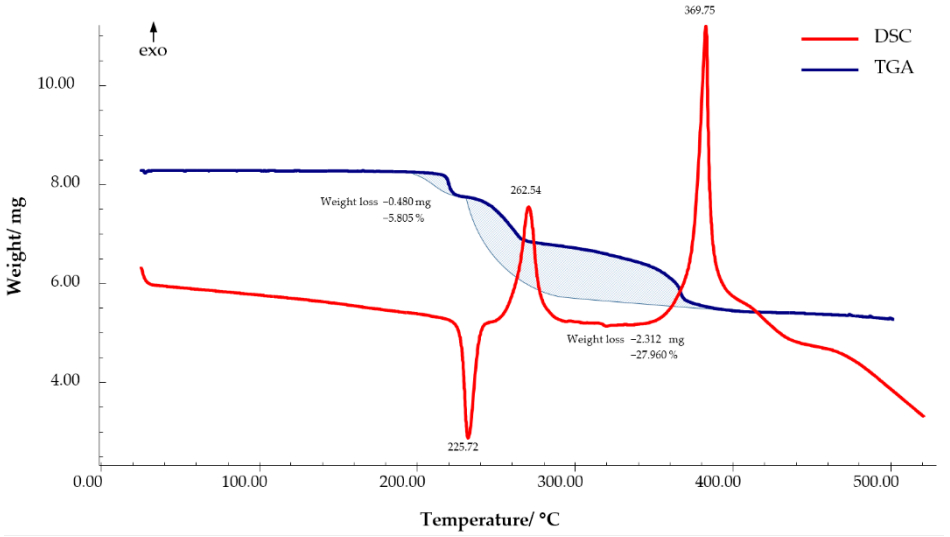


Figure 8. Thermal analyses (thermogravimetry with insert of differential scanning calorimetry) of $[Cd(NO_3)(pfb)(phen)]_n$ (**2**). Blue—TGA curve, Red—DSC curve.

According to synchronous TG analysis, compound **1** is less heat stable than compound **2**. $[Cd(NO_3)(pfb)(phen)]_n$ (**2**) starts to decompose at a much higher temperature. Thermo-

dynamic stability is influenced by factors such as coordination environment [32], number of ligands [33], and numerous inter- and intramolecular hydrogen bonds [32]. According to the X-ray data, the replacement of one pfb by a nitrate leads to changes in the crystal structure and to an increase in the number of π···π, C···C, F···F and CH···O non-covalent interactions. As a result, the crystal density increases, which is manifested in an increase in the thermodynamic stability of compound **2**, which begins to decompose at temperatures above 198 °C.

4. Conclusions

The influence of the ratio of arene and fluoroarene fragments, as well as steric factors on the structures and crystal packages of carboxylate and nitrate-carboxylate complexes of Cd, {CdTb} and Cu with anions of pentafluorobenzoic and 4-allyl-2,3,5,6-tetrafluorobenzoic acids and 1,10-phenanthroline have been shown. For cadmium and copper complexes, it was found that the partial replacement of pfb or Afb anions with compact NO_3^- anions leads to a reduction in steric hindrance, a more effective overlap of aromatic fragments, considerable changes in the geometry of complexes and the formation of denser packages. The lower thermal stability of pentafluorobenzoate compared to nitrate-pentafluorobenzoate was also revealed during the simultaneous thermogravimetric analysis of cadmium complexes, which indicates the formation of a denser package with a large number of non-covalent interactions. In the case of heterometallic pentafluorobenzoate {CdTb} polymers, due to the irregularity in the alternation of arene and perfluoroarene fragments, the replacement of part of the pentafluorobenzoate anions with nitrate anions leads only to local structural changes. It is shown that π···π interactions constitute the main contribution to the stabilization of complex structures, and in the case of cadmium compounds, they stabilize polymer structures.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/cryst13040678/s1, Scheme S1 (synthetic data), Figures S1–S3 (IR spectra), Tables S1–S3, Figures S4–S16 (structural data).

Author Contributions: Conceptualization, validation, A.A.S. and M.A.S.; methodology, M.A.S. and D.S.Y.; formal analysis, M.A.S., A.E.B., J.K.V. and L.M.E.; investigation, M.A.S., A.S.C. and A.E.B.; writing—original draft preparation, M.A.S., A.A.S. and A.S.C.; writing—review and editing, I.L.E., A.S.C. and J.K.V.; supervision, I.L.E. All authors have read and agreed to the published version of the manuscript.

Funding: The study was supported by the Russian Science Foundation grant No. 22-73-10192.

Data Availability Statement: Supplementary crystallographic data for the compounds synthesized are given in CCDC numbers 2237100 (**2**), 2237102 (**4**), 2237101 (**5**), 2237103 (**6**); These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (accessed on 1 April 2023).

Acknowledgments: X-ray diffraction analysis, CHN and IR-spectral analyzes were performed using the equipment at the Center for Collective Use of the Kurnakov Institute RAS, which operates with the support of the state assignment of the IGIC RAS in the field of fundamental scientific research.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Itoh, T.; Kondo, M.; Kanaike, M.; Masaoka, S. Arene–perfluoroarene interactions for crystal engineering of metal complexes: Controlled self-assembly of paddle-wheel dimers. *CrystEngComm* **2013**, *15*, 6122–6126. [CrossRef]
2. Cockcroft, J.K.; Rosu-Finsen, A.; Fitch, A.N.; Williams, J.H. The temperature dependence of C–H· · · F–C interactions in benzene: hexafluorobenzene. *CrystEngComm* **2018**, *20*, 6677–6682. [CrossRef]
3. Lee, G.Y.; Hu, E.; Rheingold, A.L.; Houk, K.N.; Sletten, E.M. Arene-perfluoroarene interactions in solution. *J. Org. Chem.* **2021**, *86*, 8425. [CrossRef]
4. Hori, A.; Shinohe, A.; Yamasaki, M.; Nishibori, E.; Aoyagi, S.; Sakata, M. 1:1 Cross-assembly of two β-diketonate complexes through arene–perfluoroarene interactions. *Angew. Chem. Int. Ed.* **2007**, *46*, 7617–7620. [CrossRef] [PubMed]

5. Götz, R.J.; Robertazzi, A.; Mutikainen, I.; Turpeinen, U.; Gamez, P.; Reedijk, J. Concurrent anion$\cdots\pi$ interactions between a perchlorate ion and two π-acidic aromatic rings, namely pentafluorophenol and 1,3,5-triazine. *Chem. Commun.* **2008**, *29*, 3384–3386. [CrossRef]
6. Itoh, T.; Kondo, M.; Sakamoto, H.; Wakabayashi, K.; Kanaike, M.; Itami, K.; Masaoka, S. Porous frameworks constructed by non-covalent linking of substitution-inert metal complexes. *J. Am. Chem. Soc.* **2020**, *142*, 1731–1734. [CrossRef]
7. Shmelev, M.A.; Gogoleva, N.V.; Ivanov, V.K.; Kovalev, V.V.; Razgonyaeva, G.A.; Kiskin, M.A.; Sidorov, A.A.; Eremenko, I.L. Heterometallic Ln(III)–Cd(II) complexes with anions of monocarboxylic acids: Synthetic approaches and analysis of structures and photoluminescence properties. *Russ. J. Coord. Chem.* **2022**, *47*, 539–556. [CrossRef]
8. Bear, J.C.; Cockcroft, J.K.; Williams, J.H. Influence of Solvent in Crystal Engineering: A Significant change to the order–disorder transition in ferrocene. *J. Am. Chem. Soc.* **2020**, *142*, 1731–1734. [CrossRef]
9. Sinnwell, M.A.; Baltrusaitis, J.; MacGillivray, L.R. Combination of argentophilic and perfluorophenyl-perfluorophenyl interactions supports a head-to-head [2 + 2] photodimerization in the solid state. *Cryst. Growth Des.* **2015**, *15*, 538–541. [CrossRef]
10. Kong, Y.-J.; Li, P.; Han, L.-J.; Fan, L.-T.; Li, P.-P.; Yin, S. Two cadmium(II) fluorous coordination compounds tuned by different bi pyridines. *Acta Cryst.* **2017**, *C73*, 424–429.
11. Shmelev, M.A.; Gogoleva, N.V.; Kuznetsova, G.N.; Kiskin, M.A.; Voronina, Y.K.; Yakushev, I.A.; Ivanova, T.M.; Nelyubina, Y.V.; Sidorov, A.A.; Eremenko, I.L. Cd(II) and Cd(II)–Eu(III) complexes with pentafluorobenzoic acid anions and n-donor ligands: Synthesis and structures. *Russ. J. Coord. Chem.* **2020**, *46*, 557–572. [CrossRef]
12. Shmelev, M.A.; Kuznetsova, G.N.; Dolgushin, F.M.; Voronina, Y.K.; Gogoleva, N.V.; Kiskin, M.A.; Ivanov, V.K.; Sidorov, A.A.; Eremenko, I.L. 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. *Russ. J. Coord. Chem.* **2021**, *47*, 127–143. [CrossRef]
13. Shmelev, M.A.; Kiskin, M.A.; Voronina, J.K.; Babeshkin, K.A.; Efimov, N.N.; Varaksina, E.A.; Korshunov, V.M.; Taydakov, I.V.; Gogoleva, N.V.; Sidorov, A.A.; et al. Molecular and polymer Ln_2M_2 (Ln = Eu, Gd, Tb, Dy; M = Zn, Cd) complexes with pentafluorobenzoate anions: The role of temperature and stacking effects in the structure; magnetic and luminescent properties. *Materials* **2020**, *13*, 5689. [CrossRef]
14. Shmelev, M.A.; Kuznetsova, G.N.; Gogoleva, N.V.; Dolgushin, F.M.; Nelyubina, Y.V.; Kiskin, M.A.; Sidorov, A.A.; Eremenko, I.L. Heteroleptic cadmium(II) and terbium(III) pentafluorobenzoate-benzoate and pentafluorobenzoate-2-furancarboxylate compounds. *Russ. Chem. Bull.* **2021**, *70*, 830–838. [CrossRef]
15. Zorina-Tikhonova, E.N.; Chistyakov, A.S.; Kiskin, M.A.; Sidorov, A.A.; Dorovatovskii, P.V.; Zubavichus, Y.V.; Voronova, E.D.; Godovikov, I.A.; Korlyukov, A.A.; Eremenko, I.L.; et al. Exploitation of knowledge databases in the synthesis of zinc(II) malonates with photo-sensitive and photo-insensitive N, N′-containing linkers. *IUCrJ* **2018**, *5*, 293. [CrossRef]
16. Gromov, S.P.; Vedernikov, A.I.; Lobova, N.A.; Kuz'mina, L.G.; Basok, S.S.; Strelenko, Y.A.; Alfimova, M.V.; Howard, J.A.K. Controlled self-assembly of bis(crown)stilbenes into unusual bis-sandwich complexes: Structure and stereoselective [2+2] photocycloaddition. *New J. Chem.* **2011**, *35*, 724. [CrossRef]
17. Durand, P.-L.; Brège, A.; Chollet, G.; Grau, E.; Cramail, H. Simple and efficient approach toward photosensitive biobased aliphatic polycarbonate materials. *ACS Macro Lett.* **2018**, *7*, 250. [CrossRef] [PubMed]
18. Gong, L.L.; Feng, X.F.; Luo, F.; Yi, X.F.; Zheng, A.M. Removal and safe reuse of highly toxic allyl alcohol using a highly selective photo-sensitive metal–organic framework. *Green Chem.* **2016**, *18*, 2047. [CrossRef]
19. Oguadinma, P.O.; Rodrigue-Witchel, A.; Rebera, C.; Schaper, F. Intramolecular π-stacking in copper(I) diketiminate phenanthroline complexes. *Dalton Trans.* **2010**, *39*, 8759. [CrossRef]
20. Goldberg, A.; Kiskin, M.; Shalygina, O.; Kozyukhin, S.; Dobrokhotova, Z.; Nikolaevskii, S.; Sidorov, A.; Sokolov, S.; Timoshenko, V.; Goloveshkin, A.; et al. Tetranuclear heterometallic $\{Zn_2Eu_2\}$ complexes with 1-Naphthoate anions: Synthesis, structure and photoluminescence properties. *Chem. Asian J.* **2016**, *11*, 604. [CrossRef]
21. Koshevoy, I.O.; Krause, M.; Klein, A. Non-covalent intramolecular interactions through ligand-design promoting efficient photoluminescence from transition metal complexes. *Coord. Chem. Rev.* **2020**, *405*, 213094. [CrossRef]
22. Shmelev, M.A.; Voronina, J.K.; Evtyukhin, M.A.; Dolgushin, F.M.; Varaksina, E.A.; Taydakov, I.V.; Sidorov, A.A.; Eremenko, I.L.; Kiskin, M.A. Synthesis, structure and photoluminescence properties of Cd and Cd-Ln pentafluorobenzoates with 2,2′:6′,2′-terpyridine derivatives. *Inorganics* **2022**, *10*, 194. [CrossRef]
23. Krause, L.; Herbst-Irmer, R.; Sheldrick, G.M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Cryst.* **2015**, *48*, 3–10. [CrossRef] [PubMed]
24. Sheldrick, G.M. SHELXT—Integrated space-group and crystal-structure determination. *Acta Cryst. A* **2015**, *71*, 3. [CrossRef]
25. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Cryst. C* **2015**, *71*, 3–8. [CrossRef] [PubMed]
26. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341. [CrossRef]
27. Alvarez, S.; Avnir, D.; Llunell, M.; Pinsky, M. Continuous symmetry maps and shape classification. The case of six-coordinated metal compounds. *New J. Chem.* **2002**, *26*, 996–1009. [CrossRef]
28. Spek, A.L. PLATON SQUEEZE: A tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Cryst. C* **2015**, *71*, 9–18. [CrossRef]

29. Spackman, P.R.; Turner, M.J.; McKinnon, J.J.; Wolff, S.K.; Grimwood, D.J.; Jayatilaka, D.; Spackman, M.A. CrystalExplorer: A program for Hirshfeld surface analysis, visualization and quantitative analysis of molecular crystals. *J. Appl. Cryst.* **2021**, *54*, 1006–1011. [CrossRef]
30. Edwards, A.J.; Mackenzie, C.F.; Spackman, P.R.; Jayatilaka, D.; Spackman, M.A. Intermolecular interactions in molecular crystals: What's in a name? *Faraday Discuss.* **2017**, *203*, 93–112. [CrossRef]
31. Ge, C.; Zhang, X.; Yin, J.; Zhang, R. Weak interactions involving fluorine in suppramolecular assemblies of Cu(II) complexes. *Chin. J. Chem.* **2010**, *28*, 2083–2088. [CrossRef]
32. Bai, H.; Gao, H.; Hu, M. A Zigzag chain Cd (II) coordination polymer based on 2,4-Dinitro-benzoic acid ligand: Syntheses, structure and photoluminescence. *Adv. Mater. Res.* **2014**, *997*, 140–145. [CrossRef]
33. Jassal, A.K.; Sran, B.S.; Suffren, Y.; Bernot, K.; Pointillart, F.; Cador, O.; Hundal, G. Structural diversity and photo-physical and magnetic properties of dimeric to 1D polymeric coordination polymers of lighter lanthanide(III) dinitrobenzoates. *Dalton Trans.* **2018**, *47*, 4722–4732. [CrossRef] [PubMed]

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