ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2024, Vol. 50, No. 3, pp. 179–194. © Pleiades Publishing, Ltd., 2024.

Effect of Substituents in the Pentafluorobenzoate and 2,3,4,5- and 2,3,5,6-Tetrafluorobenzoate Anions on the Structure of Cadmium Complexes

M. A. Shmelev[a], G. A. Razgonyaeva[a], D. S. Yambulatov[a], A. G. Starikov[b], A. A. Sidorov[a, *], and I. L. Eremenko[a]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*
[b] *Research Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don, Russia*
**e-mail: sidorov@igic.ras.ru*

Received June 28, 2023; revised November 13, 2023; accepted November 20, 2023

Abstract—New cadmium 2,3,4,5-tetrafluorobenzoate (6HTfb) and 2,3,5,6-tetrafluorobenzoate (4Htfb) complexes, $[Cd(6HTfb)(H_2O)_3]_n \cdot (6HTfb) \cdot 2nH_2O$ (**I**), $[Cd_3(Phen)_2(6HTfb)_6]$ (**II**, Phen = 1,10-phenanthroline), $[Cd_2(Phen)_2(4Htfb)_4]_n \cdot 2nH_2O$ (**III**), and $[Cd(Phen)_2(4Htfb)_2]$ (**IV**), were synthesized. Analysis of the obtained results and published data demonstrated that a decrease in the number of fluorine substituents is unfavorable for the formation of coordination polymers comprising stacked alternating fluorinated and non-fluorinated aromatic moieties. In the case of 2,4,5-trifluorobenzoate complex, a typical trivial structure of the binuclear cadmium complex with ligand-shielded metal core is formed. The synthesis of 2,3,4,5- and 2,3,5,6-tetrafluorobenzoate complexes produced an intermediate situation and demonstrated that the structure of complex formation products is affected by not only the number, but also the positions of fluorine substituents. Using quantum chemical calculations, it was shown that the formation of coordination polymers requires a molecular precursor with a Chinese lantern structure stable in solutions, while the formation of unusual flattened binuclear complexes with additionally coordinated water molecules requires doubly bridged binuclear complexes able to switch to a conformation with exposed coordinatively unsaturated metal centers.

Keywords: cadmium, tetrafluorobenzoates, pentafluorobenzoates, coordination polymers, non-covalent interactions, quantum chemical calculations

DOI: 10.1134/S1070328423601486

INTRODUCTION

The chemical behavior of carboxylate complexes of 3*d* metals and cadmium has much in common. The differences are primarily related to large coordination numbers and longer bonds formed by cadmium ions with the donor atoms of the coordination environment. This, in turn, leads to more pronounced tendency of cadmium to produce coordination polymers compared to 3*d* metals [1–3]. This tendency can be markedly enhanced by contribution of non-covalent interactions to stabilization of polymer structures [4, 5] or suppressed by steric hindrance [6–10]. Stacking interactions of arene and perfluoroarene moieties can be mentioned as a type of non-covalent interactions. These interactions have been studied in relation to co-crystallized hexafluorobenzene—benzene and other arene—perfluoroarene mixtures [11–13]. In our previous studies, non-covalent contacts similar to those in the above-mentioned co-crystallized organic compounds were detected upon simultaneous coordination of heterocyclic aromatic *N*-donor ligands and pentafluorobenzoate anions to the same metal ion [14–17]. The ligand attachment to metal centers gives rise to a larger structural diversity compared to that for co-crystallized free organic molecules, and the generation of specified combinations of different aromatic moieties becomes controlled to a much greater extent. Combining pentafluorobenzoate anions and *N*-donor aromatic ligands in homo- and heterometallic cadmium complexes results, most often, in proximate positions and parallel (stacked) arrangement of the aromatic moieties, which in turn exposes the metal centers and ends in the formation of coordination polymers of various compositions and structures [14–17]. A specific feature of these polymers is that they are formed by monomeric units with a composition characteristic of known molecular complexes [18–24]. However, these building blocks have a completely different structure and are distorted in such a way that the ligands do not interfere with the formation of the coordination polymer chain; they are flattened and preorganized to form the polymer structure. It is quite clear that such flattened moieties cannot exist as stable molecular complexes, since the metal centers at the chain ends will be coordinatively unsaturated. A vivid example is provided by cadmium 2,3,4,5-tetrafluorobenzoate (6Htfb) complexes, $[Cd_2(H_2O)_2\text{-}(Phen)_2\text{-}(6Htfb)_4]$ and $[Cd_2(H_2O)_2(Quin)_2(6Htfb)_4]$ (Phen = 1,10-phenanthroline; Quin = quinoline), in which the aromatic rings of the ligands are parallel, and the binuclear metal groups $\{Cd_2(Hhen)_2(6Htfb)_4\}$ and $\{Cd_2(Quin)_2(6Htfb)_4\}$ are structurally similar to the pentafluorobenzoate moieties [14]. However, instead of coordination polymer formation, coordination of water molecules to the exposed metal centers took place to give binuclear molecular complexes.

Analysis of the structure of complexes based on X-ray diffraction data provides information on the molecular geometry in the crystal, but it is not always able to explain why the presence of identical structural motifs and a very similar composition of compounds may result in absolutely different molecular structures. Quantum chemical calculations can be used to determine the structure of an isolated molecule, i.e., they can characterize other possible isomers or conformations, some of which can exist, for example, in solution and in the gas phase. Identification of these structures by computational methods may give an explanation to experimental results. Therefore, quantum chemical calculations performed in parallel with the synthesis and structural studies of new compounds act, in fact, on a par with other physical methods by visualizing the states of molecules that are not always detectable experimentally. The purpose of our work is to analyze the experimental data and find out the possible causes for the formation of compounds similar to pentafluorobenzoate coordination polymers using results of chemical experiments and quantum chemical calculation and to explain the difference between the structures of pentafluorobenzoate, 2,3,4,5-tetrafluorobenzoate and 2,3,5,6-tetrafluorobenzoate complexes.

EXPERIMENTAL

All operations related to the synthesis of complexes **I**, **III**, and **IV** were carried out in air using distilled water and ethanol (96%). Product **II** was synthesized and isolated in anhydrous medium using the standard Schlenk technique; toluene (reagent grade, Khimmed) was dried over sodium metal, stored over sodium benzophenone complex, and withdrawn by condensation immediately prior to the synthesis. New compounds were synthesized using the following reactants: $Cd(NO_3)_2 \cdot 4H_2O$ (99%, Acros organics), KOH (analytical grade), 2,3,4,5-tetrafluorobenzoic acid (H(6Htfb), 98%, P&M Invest), 2,3,5,6-tetrafluorobenzoic acid (H(4Htfb), 98%, P&M Invest), Phen (99%, Alfa Aesar). $Cd(OH)_2$ was prepared by the reaction between stoichiometric amounts of KOH and $Cd(NO_3)_2 \cdot 4H_2O$ in water.

IR spectra were measured on a Spectrum 65 (Perkin Elmer) FTIR spectrometer in the attenuated total reflection (ATR) mode in the frequency range of 4000–400 cm^{-1}. Elemental analysis was performed on a EuroEA 3000 CHNS analyzer (EuroVector).

Synthesis of $[Cd(6Htfb)(H_2O)_3]_n \cdot n(6Htfb) \cdot 2nH_2O$ (I). H(6Htfb) (0.795 g, 4.098 mmol) was added to a suspension of freshly precipitated $Cd(OH)_2$ (0.300 g, 2.049 mmol) in water (30 mL). The reaction mixture was stirred until $Cd(OH)_2$ completely dissolved; then the resulting solution was left to evaporate at room temperature. The colorless crystals that precipitated after 2 days were separated on a paper filter. The yield of compound **I** was 99.6% (1.017 g) based on $Cd(OH)_2$.

For $C_{14}H_{10}O_8F_8Cd$

Anal. calcd., %	C, 29.5	H, 1.8
Found, %	C, 29.8	H, 2.0

IR (ATR; ν, cm^{-1}): 3405 m, 1526 s, 1472 m, 1400 s, 1270 m, 1194 m, 1106 m, 1034 s, 924 m, 880 m, 780 s, 713 m, 626 m, 529 m, 432 m.

Synthesis of $[Cd_3(Phen)_2(6Htfb)_6]$ (II). Anhydrous cadmium 2,3,4,5-tetrafluorobenzoate was prepared from cadmium tetrafluorobenzoate **I** by heating at 100°C for 10 h in a dynamic vacuum. Weighed portions of anhydrous cadmium 2,3,4,5-tetrafluorobenzoate (0.498 g, 1 mmol) and 1,10-phenanthroline (0.180 g, 1 mmol) were placed into a glass tube and degassed in a dynamic vacuum for 30 min. Toluene (30 mL) was condensed into the tube, and the tube was sealed and kept in an oil bath at 120°C until the reactants completely dissolved (5 h). The reaction mixture was cooled down (10°C/h) to 90°C and the formation of crystals was observed. Maintenance at a constant temperature (3 h) and further heating of the reaction mixture to room temperature resulted in the formation of parallelepiped-shaped colorless crystals. The yield of compound **II** was 0.495 g (80%) based on anhydrous cadmium 2,3,4,5-tetrafluorobenzoate.

For $C_{66}H_{22}N_4O_{12}F_{24}Cd_3$

Anal. calcd., %	C, 42.7	H, 1.2	N, 3.0
Found, %	C, 42.6	H, 1.1	N, 2.9

IR (ATR; ν, cm^{-1}): 3079 w, 3066 w, 1639 w, 1585 m, 1520 s, 1476 m, 1429 m, 1396 m, 1368 m, 1349 m, 1326 m, 1286 w, 1261 w, 1255 m, 1225 w, 1207 w, 1183 w, 1144 m, 1095 m, 1026 s, 994 w, 965 w, 910 m, 883 m, 864 m, 843 m, 801 m, 797 m, 771 s, 753 s, 725 vs, 704 s, 692 m, 639 w, 618 w, 555 w, 521 w, 509 w, 490 w, 471 w, 456 w, 444 w, 423 m, 406 m.

Synthesis of $[Cd_2(Phen)_2(4Htfb)_4]_n·2nH_2O$ (III). H(4Htfb) (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 until the reactants completely dissolved. The resulting colorless solution was evaporated to dryness, and the residue was dissolved in EtOH (25 mL) at 70°C. Phen (0.062 g, 0.342 mmol) was added to the resulting solution, and the mixture was stirred for 10 min at 70°C. The colorless solution was kept at room temperature to slowly evaporate. The colorless crystals, suitable for X-ray diffraction, that formed after 5 days were separated by decantation, washed with cold EtOH ($T \approx$ 5°C), and dried in air. The yield of compound **III** was 0.180 g (75.6%) based on $Cd(OH)_2$.

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

Anal. calcd., %	C, 44.8	H, 1.7	N, 4.0
Found, %	C, 44.5	H, 1.8	N, 3.8

IR (ν, cm^{-1}): 3080 w, 1976 w, 1582 s, 1518 s, 1473 s, 1429 s, 1396 s, 1361 s, 1322 m, 1286 w, 1255 s, 1224 w, 1204 m, 1184 w, 1143 m, 1096 m, 1025 s, 909 m, 883 m, 864 m, 844 s, 802 s, 795 s, 772 s, 754 s, 726 s, 704 s, 692 m, 639 w, 619 w, 598 w, 575 w, 552 w.

Synthesis of $[Cd(Phen)_2(4Htfb)_2]$ (IV) was performed by a procedure similar to that used for **III** using Phen (0.124 g, 0.685 mmol). The colorless solution was kept at room temperature to slowly evaporate. The colorless crystals, suitable for X-ray diffraction, that formed after 2 days were separated by decantation, washed with cold EtOH ($T \approx$ 5°C), and dried in air. The yield of compound **IV** was 0.202 g (68.9%) based on $Cd(OH)_2$.

For $C_{76}H_{36}N_8O_8F_{16}Cd_2$

Anal. calcd., %	C, 53.1	H, 2.1	N, 6.5
Found, %	C, 53.3	H, 1.9	N, 6.1

IR (ν, cm^{-1}): 3854 w, 3838 w, 3801 w, 3674 w, 2987 m, 2971 m, 2900 m, 2360 w, 2341 w, 2161 m, 1978 w, 1741 w, 1717 w, 1588 s, 1519 m, 1470 s, 1420 s, 1392 s, 1376 s, 1262 m, 1222 m, 1142 m, 1093 s, 1077 m, 1065 s, 1049 s, 1026 w, 907 m, 881 m, 862 m, 845 s, 799 w, 769 m, 727 s, 692 m, 636 s, 620 m, 576 w, 566 w, 556 m.

Single crystal X-ray diffraction study of compounds **I**–**IV** was carried out on a Bruker Apex II diffractometer or a Bruker D8 Venture diffractometer equipped with a CCD detector (MoK_{α}, $\lambda = 0.71073$ Å, graphite monochromator) [25]. The absorption corrections for all compounds were applied semiempirically by the SADABS program [26]. The structures were solved by direct methods and refined by full-matrix least-squares calculations in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of organic ligands were generated geometrically and refined in the riding model; OH-group hydrogen atoms were located from difference Fourier maps. The calculations were carried out using the SHELX program package [27] with OLEX2 [28]. The polyhedron geometry was determined using the continuous shape measures (CShMs) and the SHAPE 2.1 program [29]. CShMs show the deviation of atom coordinates in the coordination environment of the metal ion from the vertices of ideal polyhedra. Full coincidence of the polyhedron geometry with the ideal shape corresponds to zero Cshm. The crystallographic data and structure refinement details for **I**–**IV** are summarized in Table 1; selected distances and angles of intra- and intermolecular interactions are given in Tables 2–4; and the major distances and angles are in Table 5.

The atom coordinates and other characteristics of compounds **I**–**IV** are deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2090783, 2090788, 2090778, and 2090782, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Quantum chemical calculations were performed using the Gaussian16 program [30] by the density functional theory method (DFT) [31] with the B3LYP functional [32], which proved to be efficient in the studies of analogous binuclear metal carboxylate complexes [33–35], and split valence basis set with inclusion of Def2-TZVP polarization and diffusion functions. This provided a reasonable trade-off between the approximation level and the computation time. Due to the high stereochemical non-rigidity of the complexes, the packing effects were modeled using the D3BJ Grimme empirical corrections [36] and the CAM-B3LYP functional [37], which provides description of long-range interactions, and a combination of these approaches. The structures of the complexes discussed here were calculated using full geometry optimization without symmetry constraints and with wave function stability check. In the preliminary stage, the calculations were performed with the Def2-SVP basis set; the calculated structures were obtained using the Def2-TZVP split valence basis set. The graphical images of molecular structures were obtained using the ChemCraft program [38].

RESULTS AND DISCUSSION

Previously, we showed that the $\{Cd_2(Phen)_2(6Htfb)_4\}$ moiety in the 2,3,4,5-tetrafluorobenzoate complex $[Cd_2(H_2O)_2(Phen)_2(6Htfb)_4]$ is almost structurally identical to the binuclear moiety of the pentafluorobenzoate coordination polymer $\{Cd_2(Phen)_2(Pfb)_4\}_n$ [14]. It appeared of interest to find out whether the absence of water in the reaction mixture would lead to isolation of a compound similar to the pentafluorobenzoate polymer. We made attempts to prepare cadmium 2,3,4,5-tetrafluorobenzoate com-

Table 1. Crystallographic data and structure refinement details for **I**–**IV**

Parameters	**I**	**II**	**III**	**IV**
Molecular formula	$C_{14}H_{10}CdF_8O_8$	$C_{66}H_{22}Cd_3F_{24}N_4O_{12}$	$C_{26}H_{12}CdF_8N_2O_5$	$C_{38}H_{18}CdF_8N_4O_4$
M	570.62	1856.07	696.78	858.96
T, K	100(2)	150(2)	296(2)	100(2)
System	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/c$
a, Å	37.387(3)	21.6817(10)	7.081(3)	12.916(3)
b, Å	6.5416(6)	20.8869(9)	13.396(3)	14.6722(17)
c, Å	14.2292(12)	14.4460(7)	14.016(5)	17.805(3)
α, deg	90	90	108.103(11)	90
β, deg	103.242(4)	94.028(2)	102.634(18)	91.588(8)
γ, deg	90	90	99.993(16)	90
V, Å^3	3387.5(5)	6525.9(5)	1190.7(8)	3372.9(9)
Z	8	4	2	4
ρ(calcd.), g cm^{-3}	2.238	1.889	1.943	1.692
μ, mm^{-1}	1.422	1.104	1.025	0.741
θ_{max}, deg	24.403	25.996	24.407	25.998
T_{min}/T_{max}	0.5456/0.7461	0.689/0.782	0.749/0.904	0.5549/0.7453
Number of measured reflections	11601	25864	6336	24299
Number of unique reflections	2771	6383	3790	6546
Number of reflections with $I > 2\sigma(I)$	2349	5916	3140	4242
R_{int}	0.0555	0.0215	0.0384	0.1064
Number of refined parameters	691	989	6135	667
GOOF	1.049	1.042	1.077	0.965
R_1 ($I > 2\sigma(I)$)	0.0360	0.0233	0.0566	0.0526
wR_2 ($I > 2\sigma(I)$)	0.0901	0.0591	0.1381	0.1505
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	–0.835/1.672	–0.394/0.478	–0.846/1.141	–0.822/0.884

plex with 1,10-phenanthroline from the anhydrous salt and anhydrous acetonitrile under inert atmosphere. Anhydrous cadmium 2,3,4,5-tetrafluorobenzoate was prepared by heating $[Cd(6Htfb)(H_2O)_3]_n \cdot n(6Htfb) \cdot 2nH_2O$ (**I**) at 100°C for 10 h in a dynamic vacuum. However, the removal of water molecules from the reaction mixture led to the formation of the molecular trinuclear complex $[Cd_3(Phen)_2(6Htfb)_6]$ (**II**).

The systems studied here, formed under the influence of arene—perfluoroarene stacking interactions, are very sensitive to any changes in the structures of the fluorinated benzoic acid derivative and the N-donor ligand. According to published data, the structuring effects of the arene—perfluoroarene noncovalent interactions decrease with decreasing number of fluorine atoms in the aromatic moiety. The introduction of fluorine atoms decreases the π-density in the ring; as a result, stacking interactions with π-saturated systems containing no electron-withdrawing substituents or containing donor substituents become very favorable. Indeed, 2,4,5-trifluorobenzoate [39] and 2-fluorobenzoate [40] complexes have a typical doubly bridged binuclear structure $[Cd_2(Phen)_2(\mu\text{-}OOCR)_2(OOCR)_2]$, like that of the benzoate complex [41]. It is obvious that a decrease in the number of fluorine atoms in the carboxylate anion reduces the strength of non-covalent interactions between the fluorinated and unsubstituted aromatic moieties. These interactions are no longer able to ensure a parallel arrangement of the coordinated 1,10-phenanthroline molecules and the aromatic groups of the carboxylate anions in the $[Cd_2(L)_2(OOCR)_4]$ complexes, and effects related to the formation of polymer structures are no longer manifested. From this standpoint, 2,3,4,5-tetrafluorobenzoate complexes illustrate the boundary conditions for specific structuring effects. However, one could expect that not only the number, but also positions of fluorine substituents would affect the structure of the compounds. Hence, it was reason-

Table 2. Parameters of hydrogen bonds in the crystals of **I**–**IV**

Hydrogen bond	D–H, Å	H···A, Å	D···A, Å	% of the sum of Wan der Waals radii of D and A	DHA angle, deg
			I		
O(5)–H(5A)···O(4)	0.88	1.97	2.730(4)	89.8	144
O(5)–H(5B)···O(3)	0.88	1.97	2.771(4)	91.1	150
O(6)–H(6A)···O(5)	0.83	1.98	2.778(5)	91.4	162
O(6)–H(6B)···O(3)	0.83	1.80	2.620(5)	86.2	170
O(7)–H(7A)···O(2)	0.87	1.90	2.712(4)	89.1	154
O(7)–H(7B)···O(1)	0.88	1.93	2.775(4)	91.1	160
O(8)–H(8)···O(4)	0.82	1.94	2.738(4)	90.0	166
O(9)–H(9)···O(4)	0.72	2.09	2.790(5)	91.7	165
C(14)–H(14)···O(3)	0.95	2.41	2.734(6)	84.7	100
			II		
C(21B)–H(21B)···O(6)	0.95	2.34	2.688(5)	83.2	101
C(22)–H(22)···O(1)	0.95	2.59	3.146(3)	97.5	117
C(23)–H(23)···F(17B)	0.95	2.53	3.010(4)	94.9	112
			III		
O(5)–H(5A)···O(4)	0.85	1.90	2.746(9)	90.3	173
C(12)–H(12)···O(5)	0.93	2.28	3.188(9)	99.0	165
			IV		
C(17)–H(17)···O(4)	0.95	2.41	3.099(6)	95.9	129
C(32)–H(32)···F(3)	0.95	2.40	2.960(6)	93.3	117

Table 3. System of π···π interactions in the crystal packing of **I**–**IV***

Contact	Cg···Cg, Å	Cg···Perp, Å	α, deg	β, deg	γ, deg
			I		
6Htfb···6Htfb	3.659(3)	3.200(2)	3.9(3)	25.6	29.0
			II		
Phen···Phen	3.405(1)	3.404(1)	0.0(1)	1.4	1.4
Phen···Phen	3.535(7)	3.287(5)	3.0(6)	21.6	21.6
6Htfb···6Htfb	3.599(1)	3.388(1)	0.8(1)	18.9	17.7
6Htfb···6Htfb	3.530(1)	3.423(1)	1.1(1)	14.1	14.1
			III		
Phen···4Htfb	3.484(5)	3.386(3)	6.3(4)	17.5	13.6
Phen···4Htfb	3.622(5)	3.384(3)	6.3(4)	26.0	20.9
			IV		
Phen···Phen	3.553(3)	3.294(2)	9.5(2)	18.2	22.0
Phen···Phen	3.543(3)	3.378(2)	1.3(2)	18.9	17.6

* Cg is the centroid of aromatic rings; Perp is perpendicular to the ring plane; α is the dihedral angle between planes **I** and J; β is the vector of the Cg(**I**)–>Cg(J) or Cg(**I**)–>Me angle and normal to plane **I**; γ is the vector of the Cg(**I**)–>Cg(J) angle and normal to plane J.

Table 4. System of C–F···π contacts in the crystal packing of complexes **I**–**IV**

Contact	F···Cg, Å	F···Perp, Å	γ, deg	CFCg, deg	C···Cg, Å
			I		
C(11)–F(11)···Cg(1)	3.319(4)	3.077	21.97	100.8(3)	3.808(6)
C(28)–H(28B)···Cg(2)	3.262(8)	3.066	19.98	99.0(4)	3.746(6)
			II		
C(14)–F(10B)···Cg(3)	3.392(2)	3.327	11.18	143.6(1)	4.527(3)
C(13)–F(13)···Cg(4)	3.292(2)	3.194	13.98	91.2(1)	3.583(3)
C(20B)–F(20B)···Cg(2)	3.464(6)	3.082	27.16	171.3(5)	4.822(5)
C(20A)–F(20A)···Cg(6)	3.609(10)	3.323	22.96	66.8(6)	3.319(12)
			III		
C(6)–F(6)···Cg(6)	3.465(6)	3.210	22.14	84.0(4)	3.585(9)
C(7)–F(7)···Cg(6)	3.363(6)	3.076	23.82	85.1(4)	3.515(9)
C(14)–F(14)···Cg(2)	3.475(6)	3.264	20.05	134.6(5)	4.516(9)
			IV		
C(3)–F(3)···Cg(4)	3.406(4)	3.345	10.88	95.7(3)	3.786(6)
C(4)–F(4)···Cg(8)	3.332(5)	3.312	6.31	125.4(3)	4.264(6)
C(11)–F(11)···Cg(7)	3.247(4)	2.982	23.33	106.0(3)	3.847(6)
C(14)–F(14)···Cg(6)	3.563(4)	3.359	19.51	101.1(3)	4.050(6)

Table 5. Selected geometric characteristics of complexes **I**–**IV**

Bond	*d*, Å			
	I	**II**	**III**	**IV**
Cd–N (Phen)		2.294(2), 2.351(2)	2.298(6), 2.333(6)	2.338(4) –2.382(4)
Cd–O (H_2O)	2.296(3)–2.559(3)			
Cd–O ($RCOO^-$)	2.305(3), 2.549(3)	2.220(1)–2.651(2)	2.203(5)–2.558(5)	2.258(3), 2.279(4)
Cd···Cd	3.845	3.538	4.213	8.903
Angle	ω, deg			
CdCdCd	142.37	180.00	120.86	

able to obtain also complexes with an isomeric anion, namely, 2,3,5,6-tetrafluorobenzoate (4Htfb), in which the hydrogen atom is located in the *para* rather than *ortho* position. Unlike 6Htfb, in this case, the reaction with Phen in Cd : Phen ratio of 1 : 1 affords the coordination polymer $[Cd_2(Phen)_2(4Htfb)_4]_n \cdot 2nH_2O$ (**III**), which is not an analogue of the pentafluorobenzoate (Pfb) polymer $[Cd_2(Phen)_2(Pfb)_4]_n$ [14]. When the Cd : Phen ratio is 1 : 2, the reaction gives the molecular complex $[Cd(Phen)_2(4Htfb)_2]$ (**IV**), which has the same structure as the known pentafluorobenzoate $[Cd(Phen)_2(Pfb)_2]$ [14].

According to X-ray diffraction data, the ionic compound $[Cd(6Htfb)(H_2O)_3]_n \cdot n(6Htfb) \cdot 2nH_2O$ (**I**) is formed by the cationic chain-like 1D coordination polymer $\{Cd(H_2O)_4(6Htfb)\}_n^+$, in which the neighboring cadmium ions are bound to each other by two bridging water molecules. The cadmium environment is completed to a square antiprism (CdO_8, CShM = 1.445) via coordination of chelating 6Htfb anion and two monodentate water molecules. The positive charge of the cationic chain is counterbalanced by the 6Htfb anion, which is not coordinated to cadmium and is hydrogen-bonded to cadmium-coordinated water molecules (Table 2). The coordinated and solvate water molecules as well as oxygen and fluorine atoms of the 6Htfb anions are involved in hydrogen bonding to form a supramolecular 2D layer (Table 2, Fig. 1). The polymer chain is additionally stabilized by the C-F···π contacts (Table 4, Fig. 2) and π···π contacts between pairs of 6Htfb anions. Selected bond lengths and bond angles are presented in Table 5.

Ionic compounds with a similar composition were obtained for cadmium pentafluorobenzoate [41] and tetrafluoroterephthalate [42]. A comparison of cad-

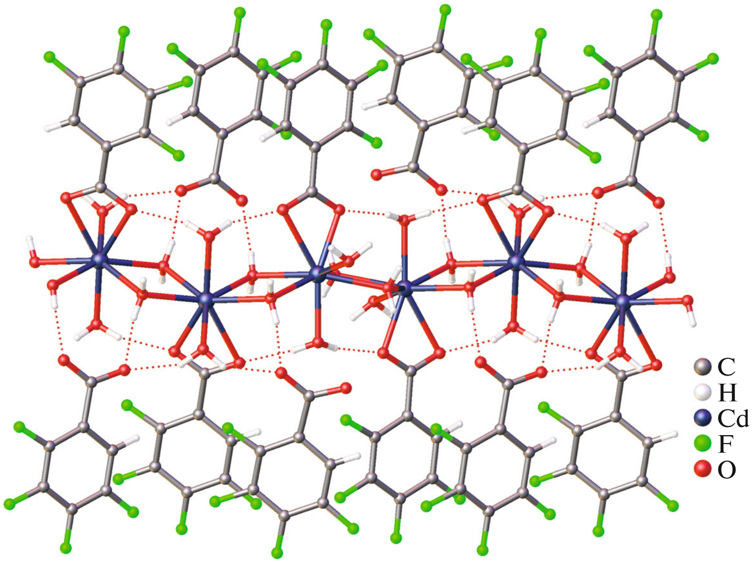

Fig. 1. Fragment of the polymer chain of compound **I**. The solvate water molecules are not shown. The dashed lines indicate hydrogen bonds.

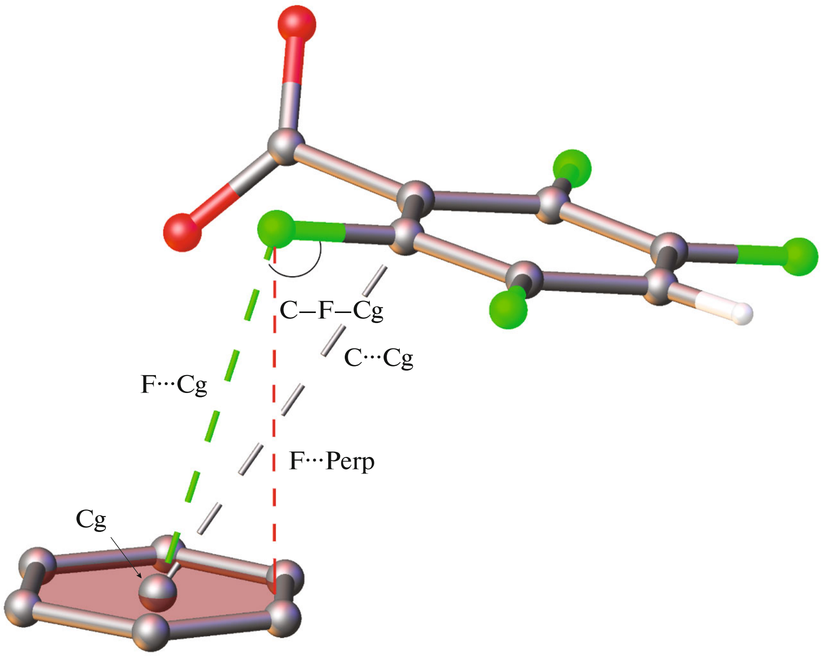

Fig. 2. Illustration of the angles and distances considered in Table 4.

mium pentafluorobenzoate (Pfb) $[Cd(Pfb)(H_2O)_3]_n \cdot n(Pfb) \cdot 2nH_2O$ and cadmium 2,3,4,5-tetrafluorobenzoate **I** demonstrated that replacement of Pfb by 6Htfb leads to shortening of the Cd–O bonds by, on average, 0.1 Å and shortening of the Cd...Cd distances in the polymer chain by 0.05 Å. There is also a greater overlap and considerable reduction of the distances between the planes of aromatic moieties in compound **I** compared with the pentafluorobenzoate complex (the distance between the centroids is 3.659(3) Å in complex **I** and 4.192(4) Å in $[Cd(Pfb)(H_2O)_3]_n \cdot n(Pfb) \cdot 2nH_2O$). However, no obvious conclusions about differences between the behaviors of pentafluorobenzoate and 2,3,4,5-tetarfluorobenzoate complexes can be drawn from the structure of the initial aqua dicarboxylates.

Complex **II** crystallizes in the monoclinic space group *C*2/*c* with the inversion center at the central

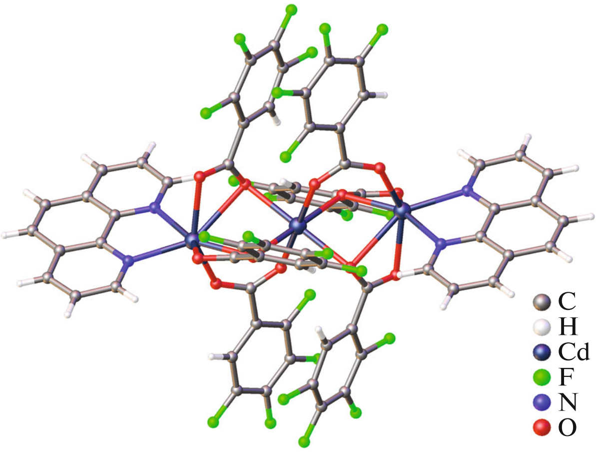

Fig. 3. Structure of molecule **II**.

cadmium ion. In the structure of **II**, each terminal cadmium ion is bonded to the central metal ion by two chelating-bridging and one bridging 6Htfb anions (Fig. 3) to give a trinuclear linear metal core (the Cd–Cd–Cd angle is 180°). The terminal cadmium atoms complete their environment to a one-capped trigonal prism by coordinating a chelating Phen molecule (CdO_5N_2, CShM = 4.483). The geometry of the central Cd ion corresponds to an octahedron (CdO_6, CShM = 0.213). Selected bond lengths and angles are summarized in Table 5.

In the packing of compound **II**, there are intermolecular π···π interactions between Phen and 6Htfb pairs (Table 3, Fig. 4), giving rise to supramolecular stacks directed along the *a* axis (Phen···Phen) and along the *c* axis (6Htfb···6Htfb). The crystal packing of **II** is additionally stabilized by a number of C–F···π, C–F···H, and C–H···O contacts giving a supramolecular framework structure (Tables 2, 4).

According to CCDC, the formation of trinuclear complexes is not highly typical of cadmium complexes with monocarboxylic acid anions and 1,10-phenatroline or its derivatives; this is also true for 3*d*-metal complexes. Previously, only one example of a trinuclear complex with a 1,10-phenanthroline derivative was described, namely, $[Cd_3(L)_2(3,5\text{-}NO_2bz)_6]$ (3,5-NO_2bz = 3,5-dinitrobenzoate anion, L = 2-(3-pyridyl)imidazo[4,5-f]-1,10-phenanthroline) [43]). Trinuclear complexes $[Cd_3(L)_2(OOCR)_6]$ ($OOCR^-$ = 9-anthracencarboxylate anion, L = methanol or ethanol) in which the cadmium environment is completed via coordination of methanol or ethanol molecules are also known [44].

It should be pointed out that a triply bridged structure is formed in almost all cadmium or 3*d*-metal car-

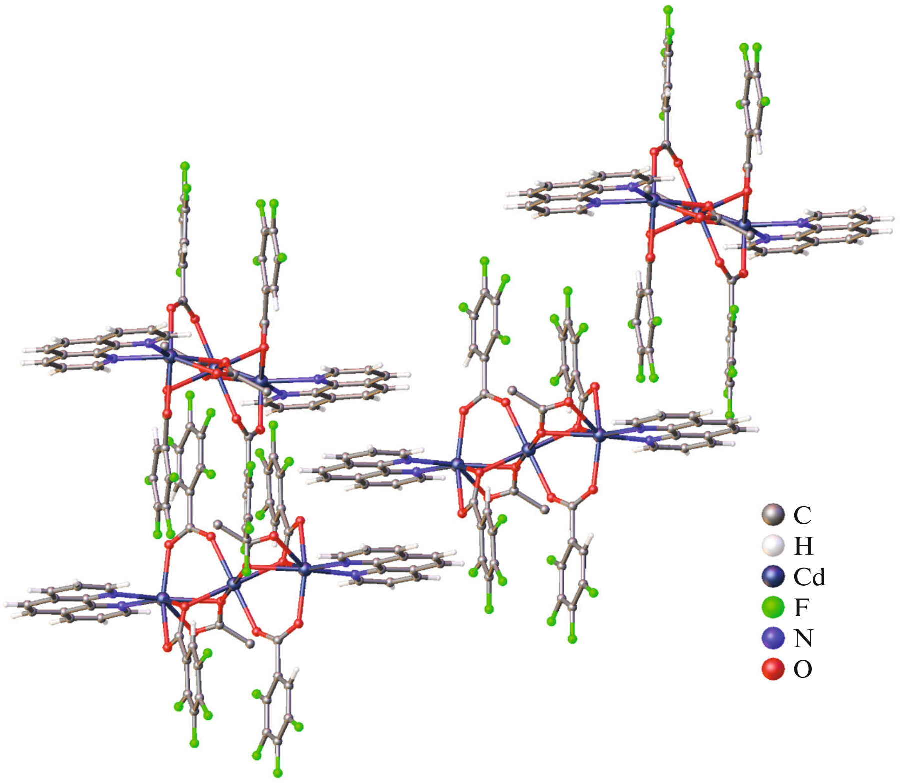

Fig. 4. Fragment of the crystal packing of complex **II**. Only aromatic moieties involved in π···π interactions are shown.

boxylate complexes where the central position in the linear trinuclear metal core is occupied by a magnesium or alkaline earth metal ion [8, 45–48].

Coordination polymer **III** crystallizes in the triclinic space group $P\overline{1}$. The polymer chain of **III** is composed of mononuclear $\{Cd(4Htfb)_2(Phen)\}$ moieties, which are connected by μ_3-η^2: η^2-4Htfb anions (Fig. 5). The environment of each cadmium ion is completed to a slightly distorted one-capped trigonal prism (CdN_2O_5, CShM = 4.485) via coordination of the Phen molecule and the κ^1-4Htfb anion.

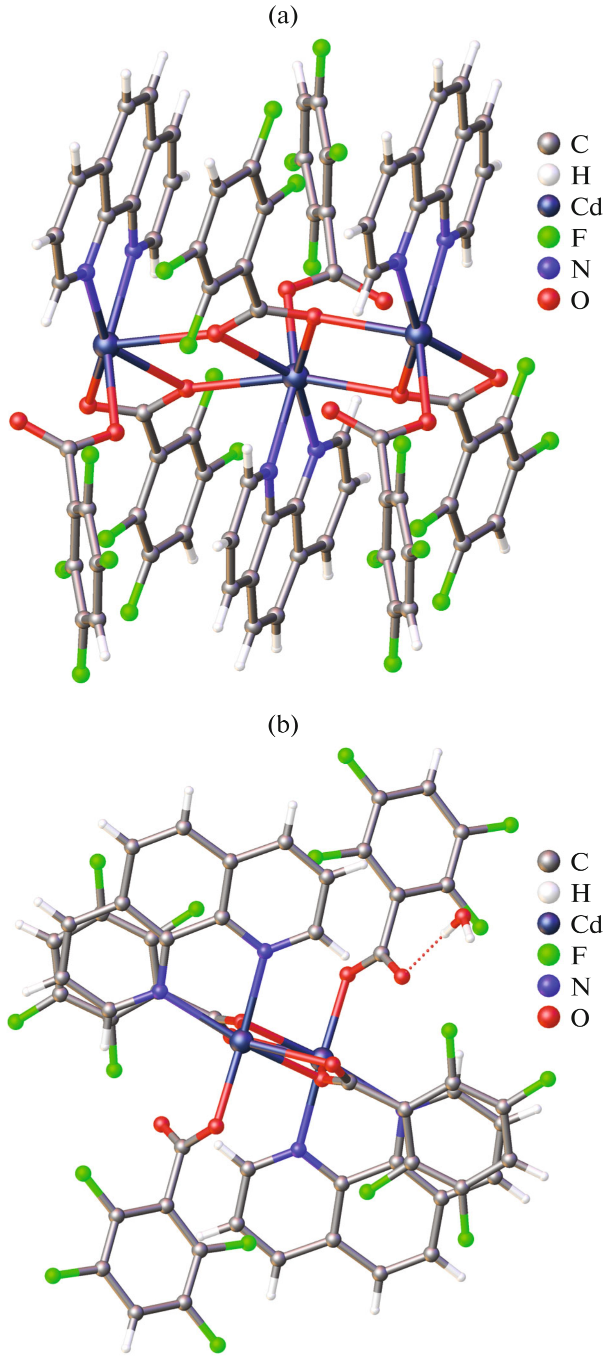

Fig. 5. Fragment of the polymer chain of complex **III**. Projections along the (a) *b* axis and (b) *a* axis are shown.

A considerable contribution to polymer chain stabilization is made by $\pi\cdots\pi$ and C–F$\cdots\pi$ interactions between the 4Htfb anions and Phen molecules directed along the *a* axis (Tables 2–4). Apparently, these interactions stabilize the structure of the coordination polymer. Selected distances and angles for complex **III** are given in Table 5. The hydrogen atoms of the Phen molecule are involved in a number of intermolecular non-covalent C–H$\cdots$O and C–H$\cdots$F interactions, giving rise to a supramolecular layered structure (Table 2). The solvate water molecule is involved in hydrogen bonding to the hydrogen atoms of 2,3,5,6-tetrafluorophenyl substituents and the oxygen atom of the uncoordinated η^1-4Htfb anion (Table 2).

A comparison of the pentafluorobenzoate polymer $[Cd_2(Phen)_2(Pfb)_4]_n$ synthesized previously with 2,3,5,6-tetrafluorobenzoate polymer **III** reveals a fairly pronounced change in the polymer chain geometry. Whereas all Pfb anions in the pentafluorobenzoate polymer are involved in the polymer chain formation and each cadmium ion is bound to neighboring metal ions via four μ_2-η^2: η^1–Pfb anions, in the case of polymer chain **III**, only half of the anions are involved in the polymer chain formation and each cadmium ion is connected in the polymer chain by three μ_3-η^2: η^2–4Htfb anions. Also, transition from the pentafluorobenzoate to 2,3,5,6-tetrafluorobenzoate polymer is accompanied by shortening of the Cd...Cd distance (the Cd...Cd distance is 3.925(2) Å for **III** and 4.008(1) Å for $[Cd_2(Phen)_2(Pfb)_4]_n$) and by a decrease in the Cd–Cd–Cd angle from 120.90(4) for **III** to 136.48(1) for $[Cd_2(Phen)_2(Pfb)_4]_n$. In the case of 2,3,5,6-tetrafluorobenzoate polymer **III** in comparison with $[Cd_2(Phen)_2(Pfb)_4]_n$, the arrangement of aromatic ligands leads to a significant increase in the overlap area of fluorobenzoate anions and Phen molecules and decreases the distances between the centroids of aromatic ligands by 0.3 to 3.484 Å, which may indicate the presence of stronger $\pi...\pi$ interactions. A similar structure of the polymer chain was detected in our previous study upon the replacement of half of the pentafluorobenzoate anions in the heteroanionic coordination polymer $[Cd(Phen)(Pfb)(NO_3)]_n$ by small nitrate anions [17]. The hydrogen bond formed by the solvate water molecule stabilizes the polymer chain structure in which half of 2,3,5,6-tetrafluorophenyl substituents protrudes out of the stack in which the coordinated 1,10-phenanthroline molecules alternate with aromatic substituents of the carboxylate anion. This apparently creates more favorable conditions for arene–perfluoroarene stacking, which is manifested as reduced distances between the centroids

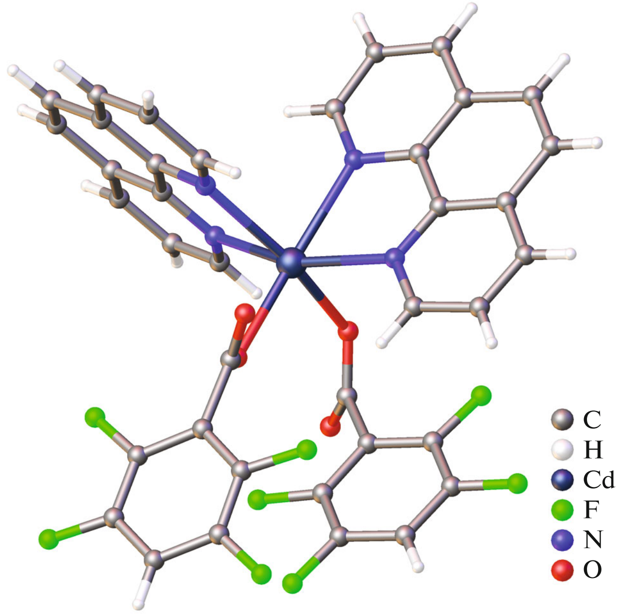

Fig. 6. Structure of molecule **IV**.

of aromatic moieties and as their greater overlap compared to that in the pentafluorobenzoate polymer $[Cd(Phen)(Pfb)_2]_n$ [14].

Treatment of **III** with one mole of 1,10-phenanthroline or the use of Cd : Phen ratio of 1 : 2 in the synthesis results in the formation of the mononuclear complex $[Cd(Phen)_2(4Htfb)_2]$ (**IV**, Fig. 6). We observed similar transformations for cadmium pentafluorobenzoates [14]. These trivial compounds similar in composition and structure are formed by Cd^{II}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} with many monocarboxylate anions [49–54]. In this case, the formation of these compounds demonstrates the relatively low stability of coordination polymers, which are easily decomposed by a stoichiometric amount of the chelating ligand.

In the structure of **IV**, the environment of the Cd ions is completed to a distorted octahedron via coordination of four N atoms of two Phen molecules and two monodentate η^1–4Htfb anions (Fig. 6, CdO_2N_4, CShM = 2.962). Selected bond lengths and angles in complex **IV** are given in Table 5. The coordinated Phen molecules are involved in the stacking interactions with two Phen aromatic moieties of two neighboring complex molecules, whereas the 4Htfb anions are not involved in the $\pi\cdots\pi$ contacts (Table 3). The crystal packing of the complex is further stabilized by a number of C–F···π, C–H···F, and C–H···O noncovalent interactions, resulting in stabilization of the supramolecular framework (Tables 2, 4). The introduction of a second Phen molecule into the cadmium coordination environment produces a geometry unfavorable for the formation of polynuclear or polymer structures, which is, apparently, attributable to lower possibility of exposure of the metal center.

The synthesis of coordination polymers described as $\{Cd_2(Phen)_2(OOCR)_4\}_n$ ($RCOO^-$ = monocarboxylate anion; L = 1,10 phenanthroline or another chelating N-donor ligand) requires certain conditions such as the absence of steric hindrance that could hamper the approach and interaction of the low-molecular species existing in the solution. Currently, there are only four reported examples of cadmium coordination polymers with 2,4-dinitrobenzoate [55], 3-(2-furyl)acrylate [56], 2,4,6-trimethylbenzoate [57], and pentafluorobenzoate [14] anions in which all carboxylate anions occupy bridging positions and are involved in the polymer chain formation. In these polymer structures, intramolecular stacking interactions between the aromatic substituents of carboxylate anions and 1,10-phenanthroline molecules are observed. Apparently, these non-covalent interactions are important for the formation and stabilization of polymer chains. It should be emphasized that, although only half of the anions participate in bridging bonds, compound **III** has an equally dense structure as the pentafluorobenzoate polymer.

The behavior of the above mentioned cadmium 2,3,4,5-tetrafluorobenzoate complexes was unexpected and required an explanation. Instead of the coordination polymer, molecular complexes of unusual composition and structure were formed. The atypical nature of their structure can be illustrated by the fact that among the enormous number of binuclear carboxylate complexes containing 1,10-phenanthroline and water, only a few such examples are known: $[M_2(H_2O)_2(Phen)_2(OOCR)_4]$ with the 2-phenylquinoline-4-carboxylate anions (M = Mn [57], Zn [58], Cd [59]) and cadmium 2,4-dihydroxybenzoate complex [7]. As a rule, the addition of water molecule to $[M_2(Phen)_2(\mu\text{-}OOCR)_2(OOCR)_2]$ gives triply bridged complexes $[M_2(Phen)_2(\mu\text{-}H_2O)(\mu\text{-}OOCR)_2(OOCR)_2]$ [60–67], while addition of a second water molecule is accompanied by monomerization to give $[M(Phen)(H_2O)(OOCR)_2]$ [19, 68–73].

In the following discussion, we use the data of the previous study devoted to analysis of the structure of isomers of binuclear cadmium carboxylate complexes with monocarboxylate anions and N-donor heterocyclic ligands [74]. In these systems, binuclear doubly bridged complexes are in equilibrium with quadruply bridged Chinese lantern-like complexes. Presumably, the formation of pentafluorobenzoate coordination polymers or binuclear 2,3,4,5-tetrafluorobenzoate complexes $[Cd_2(H_2O)_2(Phen)_2(6Htfb)_4]$ and $[Cd_2(H_2O)_2(Quin)_2(6Htfb)_4]$ is a subsequent transformation of these types of binuclear compounds.

According to quantum chemical calculations for the previously considered pivalate complexes

Table 6. Energy difference (kcal/mol) between isomers of the cadmium complexes (Chinese lantern and two bridging ligands) calculated by the DFT method with the Def2TZVP basis set

$RCOO^-$	B3LYP	CAM–B3LYP	B3LYP + D3BJ	CAM–B3LYP + D3BJ
Pentafluorophenylacetate	6.5	9.8	9.4	5.8
Pentafluorobenzoate	5.3	7.6	3.8	2.0
2,3,4,5-Tetrafluorobenzoate	6.1	7.7	–3.3	–1.1
2,4,5-Trifluorobenzoate	5.2	10.7	–3.2	–1.2

$[Cd_2L_2(Piv)_4]$ (Piv^- = pivalate anion, L = 2,4-lutidine, 2,3-cyclododecenopyridine, 2,2'-bipyridine) and the pentafluorophenylacetate (Pfaa) complex $[Cd_2(Phen)_2(\mu\text{-}Pfaa)_4]$ [74], the stabilization energy of one form relative to another one did not exceed 10 kcal/mol. Furthermore, the structure of the compound in the crystal may not coincide with the most favorable isomer for the free molecule.

A similar calculation result was obtained for the hypothetical dimer $[Cd_2(Phen)_2(\mu\text{-}Pfb)_4]$ with pentafluorobenzoate ligands, but the predicted energy difference was noticeably lower than that for the pentafluorophenylacetate $[Cd_2(Phen)_2(\mu\text{-}Pfaa)_4]$ (Table 6).

However, when the D3BJ dispersion corrections are used in the calculations, the 2,3,4,5-tetrafluorobenzoate [14] and known [39] 2,4,5-trifluorobenzoate (3,6-Htfb) complexes show a slightly, but still higher stability for isomers with two bridging ligands; furthermore, the 2,4,5-trifluorobenzoate complex in particularly this form was isolated and structurally characterized. Thus, the calculation results provide the conclusion that calculations involving the dispersion corrections to model the packing effects attest to a shift of the equilibrium between the two isomers upon a change in the number of fluorine atoms in the ligands, which is also in line with experimental data.

Although we cannot describe in detail the mechanism of formation of the final compounds the structures of which were established experimentally, it can be assumed that the conformationally flexible doubly bridged molecules with 2,3,4,5-tetrafluorobenzoate anions are flattened under the action of intramolecular stacking interactions, while the metal centers, which are thus exposed, are occupied by water molecules. Finally, doubly bridged complexes $[Cd_2(Phen)_2(6Htfb)_4]$ and $[Cd_2(Quin)_2(6Htfb)_4]$ are eliminated from the equilibrium with the quadruply bridged form, while the formation of aquated $[Cd_2(H_2O)_2(Phen)_2(6Htfb)_4]$ and $[Cd_2(H_2O)_2(Quin)_2(6Htfb)_4]$ becomes quantitative. It is of interest that these flattened molecules can be stable under certain conditions. This structure is inherent in the copper complexes $[Cu_2(Phen)_2(OOCR)_4]$ (OOCR = pentafluorobenzoate, 2-nitrobenzoate, and 3,5-dinitrobenzoate) [35, 75, 76]. The unshielded metal ion appears to be coordinatively saturated due to its tetragonal pyramidal environment.

Apparently, the decrease in the number of fluorine substituents to three no longer provides suffient energy of intramolecular non-covalent interactions for flattening of the structure, and the doubly bridged $[Cd_2(Phen)_2(3,6\text{-}Htfb)_4]$ molecule has a usual structure that ensures shielding of the metals by the ligands.

Attention should be paid to the problem of correct prediction of the geometry of the 2,3,4,5-tetrafluorobenzoate complex by various approximations (Fig. 7). The results approaching most closely the X-ray diffraction data were obtained by using a combination of the CAM-B3LYP functional with inclusion of the D3BJ Grimme dispersion corrections and the Def2-TZVP triple zeta basis set. As can be seen, neglecting short- and long-range dispersion interactions also leads to structures with coordinated water molecules; however, simultaneous inclusion of D3BJ corrections and use of CAM-B3LYP leads to a sharp compression (strengthening) of the complex caused by the formation of additional hydrogen bonds by water molecules. Probably, the observed geometry of the complexes is largely a result of interaction with solvent molecules.

The lower part of Fig. 7 shows the possible structure of this complex after removal of water molecules. In this case, too, the dispersion corrections play an important role; when they are neglected, the positions of the fluorinated phenyl groups change. In this case, the simultaneous inclusion of the D3BJ and CAM corrections also leads to a sharp compression of the complex. The cadmium atom in this complex is coordinatively unsaturated and accessible for further coordination, i.e., a binuclear complex with the structure of the above moiety will be obtained. This structure can be stabilized only when it is isolated. In the presence of donor molecules such as water in the solvent, $[Cd_2(H_2O)_2(Phen)_2(6Htfb)_4]$ or $[Cd_2(H_2O)_2(Quin)_2(6Htfb)_4]$ are formed, accumulated in the solution, and crystallize. Thus, the formation of these 2,3,4,5-tetrafluorobenzoate complexes can be explained rather simply in line with the calculation and experimental results.

Figure 8 shows some geometrical characteristics of binuclear complexes according to quantum chemical calculations. These are the complex $[Cd_2(H_2O)_2(Phen)_2(\mu\text{-}6Htfb)_2(\mu\text{-}6Htfb)_2]$, the hypothetical Chinese lantern-like pentafluorobenzoate complex $[Cd_2(Phen)_2(\mu\text{-}Pfb)_4]$, and the binuclear doubly

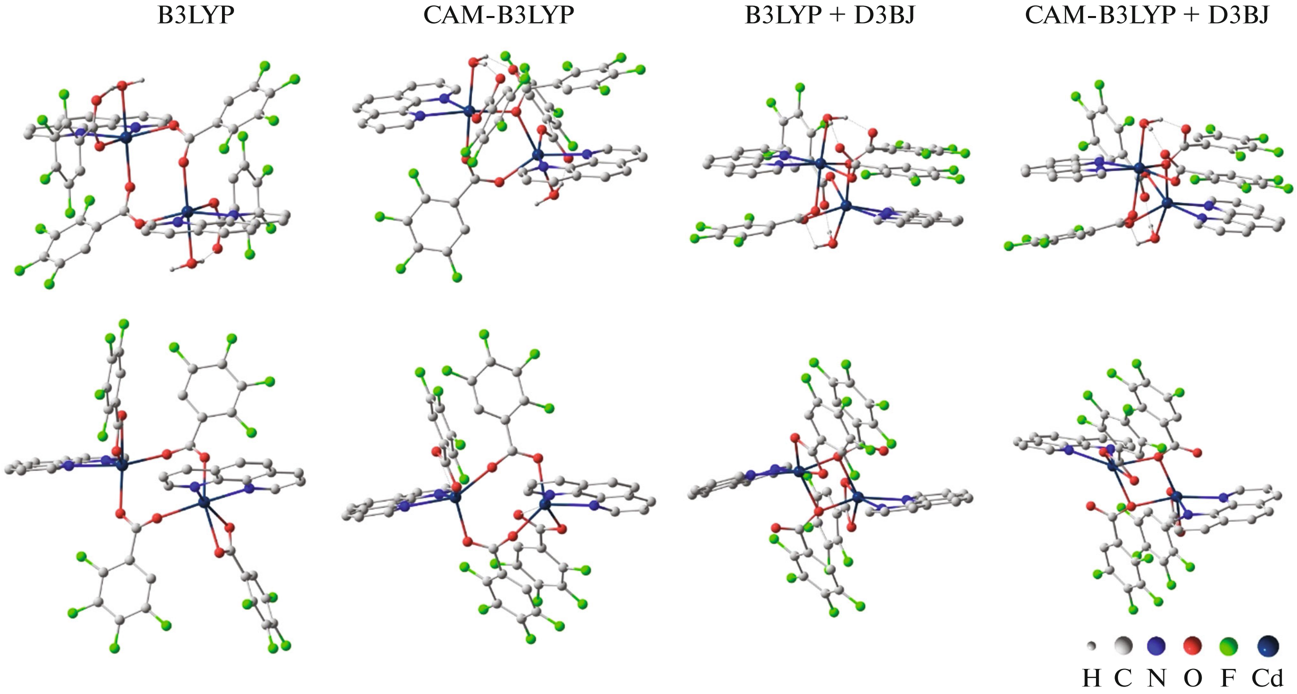

Fig. 7. Spatial structure of the dimeric cadmium 2,3,4,5-tetrafluorobenzoate complex with 1,10-phenanthroline and bis-aqua complex according to DFT calculations in various approximations. The hydrogen atoms are shown only for water molecules.

bridged 2,3,4,5-tetrafluorobenzoate complex $[Cd_2(Phen)_2(\mu\text{-}6Htfb)_2(6Htfb)_2]$. Although the existence of the binuclear cadmium complex $[Cd_2(Phen)_2(\mu\text{-}6Htfb)_2(6Htfb)_2]$ with exposed metal centers in real systems is virtually impossible, it may be assumed that in the presence of some steric restrictions, e.g., caused by substituents in positions 2 and 9 in 1,10-phenanthroline, a molecule of this type can be stabilized. The existence of conditions under which a Chinese lantern complex could be isolated seems quite conceivable. This is indicated, to an extent, by the fact that we obtained the molecular complex $[Cd_2Tb_2(Phen)_2(Pfb)_{10}]$ and coordination polymer $\{Cd_2Tb_2(Phen)_2(Pfb)_{10}\}_n$ based on the moiety of the same composition [16].

In the B3LYP/Def2-TZVP+D3BJ and CAM-B3LYP/Def2-TZVP+D3BJ approximations, the most favorable structure for the hypothetical anhydrous 2,3,4,5-tetrafluorobenzoate complex $[Cd_2(Phen)_2\text{-}(6Htfb)_4]$ is the doubly bridged structure, which may be expected to undergo a conformational transition leading to a flattened shape. As mentioned above, in order to establish the possibility of this transition in a real reaction solution, we synthesized cadmium 2,3,4,5-tetrafluorobenzoate complex with 1,10-phenanthroline in dehydrated acetonitrile and thus obtained the linear trinuclear complex $[Cd_3(Phen)_2(6Htfb)_6]$ (**II**). At first glance, this experimental result has nothing in common with the conclusion that the doubly bridged structure is more favorable. However, it should be borne in mind that calculations refer to an isolated molecule. When non-isolated molecules in this conformation appear, the metal centers will complete their coordination environment via interaction with some donor molecules, not excluding interactions with one another. Apparently, this is responsible for the observed result.

It is somewhat more difficult to account for the formation of the pentafluorobenzoate coordinating polymer $[Cd_2(Phen)_2(Pfb)_4]_n$, which we prepared previously. As was mentioned above, in the case of the hypothetical pentafluorobenzoate complex $[Cd_2(Phen)_2(Pfb)_4]$, irrespective of the approximation used, the quadruply bridged Chinese lantern structure is thermodynamically more favorable; however, according to X-ray diffraction data, the compound is a coordination polymer based on doubly bridged $[Cd_2(Phen)_2(Pfb)_4]_n$ moieties [14]. Probably, the formation of the doubly bridged isomer and its flattening to give a polymer chain occur during the solid phase formation. We encountered a somewhat similar situation when performed the quantum chemical calculations for binuclear cadmium pivalates [74]. According to the results, when the destabilization energies of doubly bridged relative to the quadruply bridged structures in the crystal are similar to those found for the pentafluorobenzoate discussed here, doubly bridged cadmium pivalates are crystallized even with 2,4-lutidine and phenanthridine, which are used in the carboxylate chemistry as classical α-substituted pyridines

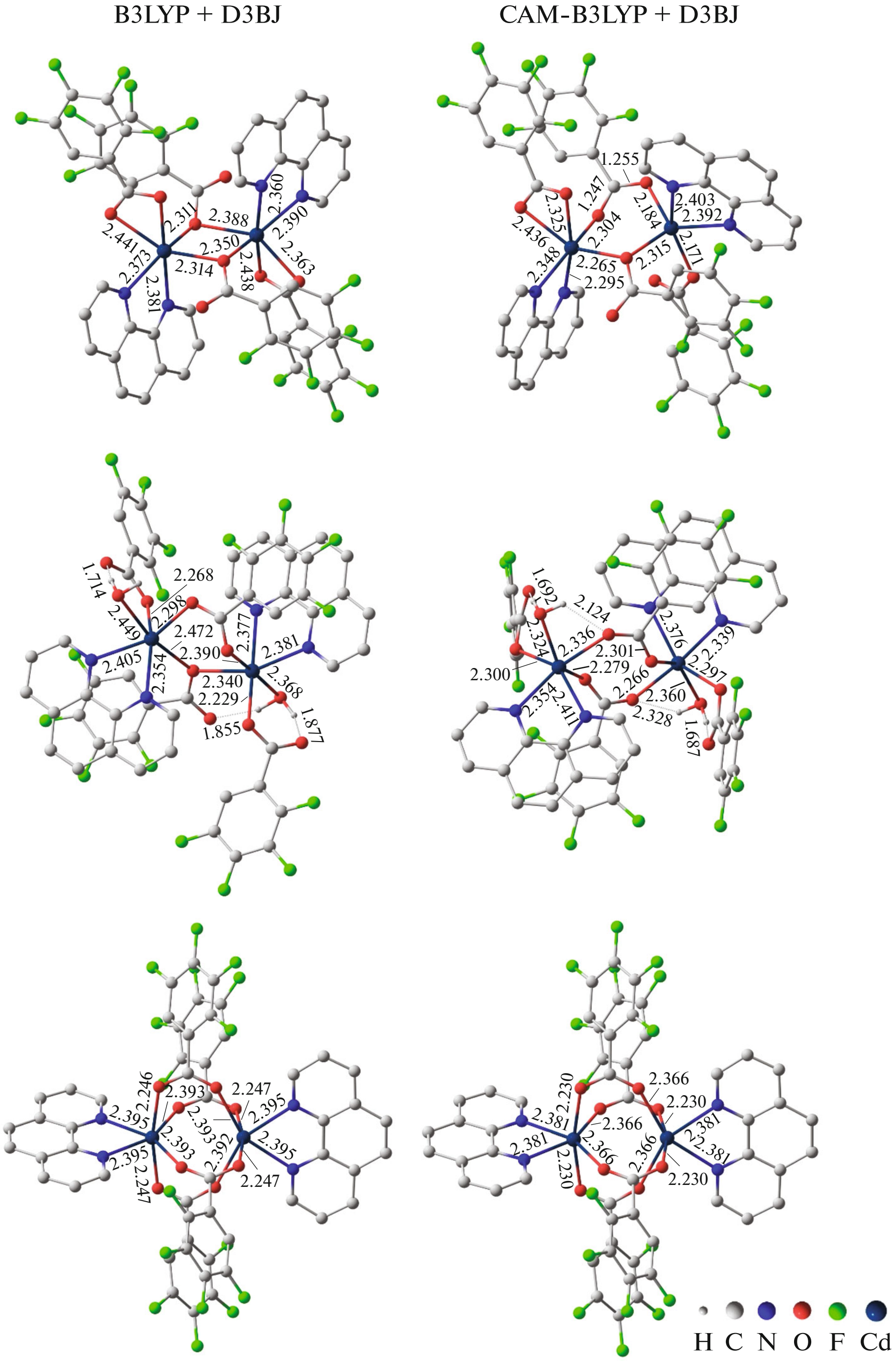

Fig. 8. Selected bond lengths in cadmium complexes according to quantum chemical data: (a) $[Cd_2(H_2O)_2(Phen)_2(\mu\text{-}6Htfb)_2(6Htfb)_2]$, (b) $[Cd_2(Phen)_2(\mu\text{-}6Htfb)_2(6Htfb)_2]$, and (c) $[Cd_2(Phen)_2(\mu\text{-}Pfb)_4]$.

to obtain quadruply bridged Chinese lantern type complexes. A similar quadruply bridged to doubly bridged isomer transition can also be assumed for the crystallization of the coordination polymer $[Cd_2(Phen)_2(Pfb)_4]_n$.

Thus, if doubly bridged and quadruply bridged isomers of binuclear complexes occur in equilibrium in solution in this type of system, a shift of the equilibrium toward the doubly bridged species can lead to the formation and subsequent crystallization of known trivial compounds with a shielded metal core. As examples, we indicated trifluorobenzoate, monofluorobenzoate, and benzoate complexes [19].

The equilibrium shift towards the quadruply bridged Chinese lantern complexes in the case of low stabilization energy relative to the doubly bridged isomer may also lead to crystallization of the doubly bridged species, as it was observed in the case of cadmium pivalate complexes with 2,4-lutidine and phenanthridine [30]. However, at a higher favorability of the flattened conformation of the doubly bridged complex, one can expect crystallization of intermediate molecules that would gather into a polymer chain. This type of transformation can be suggested for pentafluorobenzoates. As the stabilization energy of the quadruply bridged isomer increases, this isomer will be crystallized, as is the case for the cadmium pivalate complex with 2,3-cyclododecenopyridine [77] or cadmium pentafluorophenylacetate complex with 1,10-phenatroline [14].

It should be emphasized that the explanation assuming the formation of flattened binuclear moieties in the considered processes is provisional. In the case of crystallization of coordination polymers, this rather corresponds only to the fact that a compound relatively stable in solution changes its geometry to form the solid phase. If this transformation takes place in solution, one should apparently consider the formation of some intermediate able to add water or other solvent molecules.

The different structures of the pentafluorobenzoate and 2,3,5,6-tetrafluorobenzoate polymers indicate the sensitivity of the considered systems stabilized by numerous weak non-covalent interactions to any changes. Thus, the inclusion of solvated water molecules into the system of non-covalent contacts results in the formation of a structure other than the pentafluorobenzoate structure. The ease of destruction of coordination polymers by a stoichiometric amount of chelating ligand also attests to their low stabilization energies.

We attempted to give an explanation to the fact that the arene—perfluoroarene type stacking interactions may give rise to compounds with a specific structure, which in some cases are coordination polymers and in other cases are molecular complexes. Apparently, the existence of a fairly stable compound with a ligand-shielded metal core in solution, like for quadruply bridged Chinese lantern complex, is a necessary condition for polymer self-assembly, while the formation of such moieties takes place during formation of the crystalline phase. The formation of conformationally flexible structures capable of assuming a flattened conformation in solution would lead, as for 2,3,4,5-tetrafluorobenzoates, to coordination of additional molecules and stabilization of binuclear complexes. Thus, in the presence of structuring effects of the stacking interactions between the coordinated anions of fluorinated benzoic acid derivatives and 1,10-phenanthroline molecules, more extensive transformations of carboxylate complexes may take place, instead of the trivial equilibrium between the doubly bridged and quadruply bridged binuclear complexes.

ACKNOWLEDGMENTS

Single crystal and powder X-ray diffraction studies and IR spectroscopy and elemental analysis of complexes were performed using research equipment of the Center for Collective Use of Physical Investigation Methods of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, within the state assignment of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, in the field of basic scientific research.

FUNDING

Complexes **I** and **III** were synthesized and studied under the Russian Federation Presidential grant MK-94.2022.1.3; complexes **II** and **IV** were synthesized and studied within the state assignment of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, in the field of basic scientific research.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. Saxena, P. and Thirupathi, N., *Polyhedron*, 2015, vol. 98, no. 1, p. 238.
2. Pryma, O.V., Petrusenko, S.R., Kokozay, V.N., et al., *Inorg. Chem. Commun.*, 2003, vol. 6, no. 7, p. 896.
3. Zhao, Q.-H., Ma, Y.-P., Wang, Q.-H., and Fang, R.-B., *Chin. J. Struct. Chem.*, 2002, vol. 21, p. 513.
4. Shmelev, M.A., Kuznetsova, G.N., Gogoleva, N.V., et al., *Russ. Chem. Bull.*, 2021, vol. 70, no. 5, p. 830.
5. Shmelev, M.A., Chistyakov, A.S., Razgonyaeva, G.A., et al., *Crystals*, 2022, vol. 12, p. 508.
6. Yang, Y.-Q., Li, C.-H., Li, W., and Kuang, Y.-F., *Chin. J. Inorg. Chem.*, 2009, vol. 25, p. 1120.
7. Nie, J.-J., Pan, T.-T., Su, J.-R., and Xu, D.-J., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, vol. 66, p. m760.
8. Gogoleva, N.V., Shmelev, M.A., Evstifeev, I.S., et al., *Russ. Chem. Bull.*, 2016, vol. 65, p. 181.
9. Li, W., Li, C.-H., Yang, Y.-Q., and Li, Y.-L., *Chin. J. Inorg. Chem.*, 2010, vol. 26, p. 166.
10. Kuznetsova, G.N., Yambulatov, D.S., Kiskin, M.A., et al., *Russ. J. Coord. Chem.*, 2020, vol. 46, p. 553. https://doi.org/10.1134/S1070328420080047
11. Itoh, T., Kondo, M., Kanaike, M., and Masaoka, S., *CrystEngComm*, 2013, vol. 15, p. 6122.
12. Cockcroft, J.K., Rosu-Finsen, A., Fitch, A.N., and Williams, J.H., *CrystEngComm*, 2018, vol. 20, p. 6677.
13. Lee, G.Y., Hu, E., Rheingold, A.L., Houk, K.N., and Sletten, E.M., *Org. Chem.*, 2021, vol. 86, p. 8425.
14. Shmelev, M.A., Kuznetsova, G.N., Dolgushin, F.M., et al, *Russ. J. Coord. Chem.*, 2021, vol. 47, p. 127. https://doi.org/10.1134/S1070328421020068

15. Shmelev, M.A., Voronina, J.K., Evtyukhin, M.A., et al., *Inorganics*, 2022, vol. 10, p. 194.
16. Shmelev, M.A., Kiskin, M.A., Voronina, J.K., et al., *Materials*, 2020, vol. 13, no. 24, p. 5689.
17. Voronina, J.K., Yambulatov, D.S., Chistyakov, A.S., et al., *Crystals*, 2023, vol. 13, p. 678.
18. Li, J.-X. and Du, Z.-X., *J. Cluster Sci*., 2020, vol. 31, p. 507.
19. Wu, W.P., Wang, J., Lu, L., Xie, B., Wu, Y., and Kumar, A., *Russ. J. Coord. Chem*., 2016, vol. 42, p. 71.
20. Corradi, A.B., Menabue, L., Saladini, M., Sola, M., and Battaglia, L.P., *Dalton Trans*., 1992, p. 2623.
21. Nikolaevskii, S.A., Evstifeev, I.S., and Kiskin, M.A., et al., *Polyhedron*, 2018, vol. 152, p. 61.
22. Shmelev, M.A., Gogoleva, N.V., Dolgushin, F.M., et al., *Russ. J. Coord. Chem*., 2020, vol. 46, no. 7, p. 493. https://doi.org/10.1134/S1070328420070076
23. Yang, Y.-Q., Li, C.-H., Li, W., and Kuang, Y.-F., *Chin. J. Inorg. Chem*., 2010, vol. 26, p. 1890.
24. Zha, M.-Q., Li, X., and Bing, Y., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, vol. 67, p. m8.
25. *SMART (control) and SAINT (integration). Software. Version 5.0*, Madison: Bruker AXS Inc., 1997.
26. Sheldrick, G.M., *SADABS*, Madison: Bruker AXS Inc., 1997.
27. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem*., 2015, vol. 71, p. 3.
28. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., and Puschmann, H., *J. Appl. Crystallogr*., 2009, vol. 42, p. 339.
29. Casanova, D., Llunell, M., Alemany, P., and Alvarez, S., *Chem.-Eur. J*., 2005, vol. 11, p. 1479.
30. Frisch, M.J., Trucks, G.W., Schlegel, H.B., et al., *Gaussian 16. Revision A. 03*, Wallingford: Gaussian, 2016.
31. Kohn, W. and Sham, L.J., *Phys. Rev. A*, 1965, vol. 140, p. 1133.
32. Becke, A.D., *J. Chem. Phys*., 1993, vol. 98, p. 5648.
33. Nikolaevskii, S.A., Kiskin, M.A., Starikova, A.A., et al., *Russ. Chem. Bull*., 2016, vol. 65, p. 2812.
34. Nikolaevskii, S.A., Kiskin, M.A., Starikov, A.G., et al., *Russ. J. Coord. Chem*., 2019, vol. 45, no. 4, p. 273. https://doi.org/10.1134/S1070328419040067
35. Gogoleva, N.V., Shmelev, M.A., Kiskin, M.A., et al., *Russ. J. Coord. Chem*., 2021, vol. 47, no. 4, p. 261. https://doi.org/10.1134/S1070328421040035
36. Grimme, S., Ehrlich, S., and Goerigk, L.L., *J. Comput. Chem*., 2011, vol. 32, p. 1456.
37. Yanai, T., Tew, D., and Handy, N., *Chem. Phys. Lett*., 2004, vol. 393, p. 51.
38. *Chemcraft—Graphical Software for Visualization of Quantum Chemistry Computations. Version 1.8. Build 682*, https://www.chemcraftprog.com.
39. Ge, C.-H., Zhang, R., Fan, P., Zhang, X.-D., et al., *Chin. Chem. Lett*., 2013, vol. 24, p. 73.
40. Lou, Q.-Z., *Z. Kristallogr.-New Cryst. Struct*., 2007, vol. 222, p. 105.
41. Shmelev, M.A., Gogoleva, N.V., Kuznetsova, G.N., et al., *Russ. J. Coord. Chem*., 2020, vol. 46, no. 8, p. 557. https://doi.org/10.31857/S0132344X2008006X
42. Dankhar, S.S. and Nagaraja, C.M., *J. Solid State Chem*., 2020, vol. 290, p. 121560.
43. Wang, X.L., Zhang, J.X., Liu, G.C., et al., *Russ. J. Coord. Chem*., 2010, vol. 36, p. 662.
44. Bu, X.-H., Tong, M.-L., Li, J.-R., et al., *Cryst. Eng. Comm*., 2005, vol. 7, p. 411.
45. Clegg, W., Little, I.R., and Straughan, B.P., *Inorg. Chem*., 1988, vol. 27, p. 1916.
46. Clegg, W., Harbron, D.R., and Straughan, B.P., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*., 1991, vol. 47, p. 267.
47. Escobedo-Martinez, C., Lozada, M.C., and Gnecco, D., *J. Chem. Cryst*., 2012, vol. 42, p. 794.
48. Pramanik, A., Fronczek, F.R., Venkatraman, R., and Hossain, M.A., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2013, vol. 69, p. m643.
49. Necefoglu, H., Clegg, W., and Scott, A.J., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2002, vol. 58, p. m123.
50. Jin, Z.-N. and Zhang, B.-S., *Z.Kristallogr.-New Cryst. Struct*., 2018, vol. 233, p. 179.
51. Carballo, R., Covelo, B., Fernandez-Hermida, N., et al., *J. Chem. Cryst*., 2011, vol. 41, p. 1949.
52. Tunsrichon, S., Sukpattanacharoen, C., Escudero, D., et al., *Inorg. Chem*., 2020, vol. 59, p. 6176.
53. Carballo, R., Covelo, B., Garcia-Martinez, E., et al., *Appl. Organomet. Chem*., 2004, vol. 18, p. 201.
54. Sen, S., Saha, M.K., Kundu, P., et al., *Inorg. Chim. Acta*, 1999, vol. 288, p. 118.
55. Roy, S., Bauza, A., Frontera, A., et al., *CrystEngComm*, 2015, vol. 17, p. 3912.
56. Bai, H., Gao, H., and Hu, M., *Adv. Mater. Res*., 2014, vol. 997, p. 140.
57. Li, W., Li, C.-H., Yang, Y.-Q., and Li, D.-P., *Chin. J. Inorg. Chem*., 2008, vol. 24, p. 2060.
58. Li, W., Li, C.-H., Yang, Y.-Q., et al., *Chin. J. Inorg. Chem*., 2007, vol. 23, p. 2013.
59. Li, W.-W., Bing, Y., Zha, M.-Q., et al., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2011, vol. 67, p. m1464.
60. Bing, Y., Li, X., Zha, M.-Q., and Wang, D.-J., *Nano-Met. Chem*., 2011, vol. 41, p. 798.
61. Zha, M.-Q., Li, X., and Bing, Y., *J. Coord. Chem*., 2011, vol. 64, p. 473.
62. Pruchnik, F.P., Dawid, U., and Kochel, A., *Polyhedron*, 2006, vol. 25, p. 3647.
63. Liu, C.-S., Sanudo, E.C., Yan, L.-F., et al., *Transition Met. Chem*., 2009, vol. 34, p. 51.
64. Song, W.-D., Yan, J.-B., and Hao, X.-M., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2008, vol. 64, p. m919.
65. Liu, G.-C., Qu, Y., Wang, X.-L., Zhang, J.-W., et al., *Z. Anorg. Allg. Chem*., 2014, vol. 640, p. 1696.
66. Feng, S., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2008, vol. 64, p. m817.
67. Uvarova, M.A., Kushan, E.V., Andreev, M.V., et al., *Russ. J. Inorg. Chem*., 2012, vol. 57, p. 1314.
68. Gomez, V. and Corbella, M., *Eur. J. Inorg. Chem*., 2009, p. 4471.

69. Kruszynski, R., Malinowska, A., Czakis-Sulikowska, D., and Lamparska, A., *J. Coord. Chem.*, 2009, vol. 62, p. 911.

70. Shao, C.-Y., Song, S., Song, M., et al., *Chin. Chem. Res.*, 2011, vol. 22, p. 29.

71. Deng, Z.-P., Gao, S., Huo, L.-H., and Zhao, H., *Acta Crystallogr., Sect. E*: *Struct. Rep. Online*, 2007, vol. 63, p. m2694.

72. Li Zuo, Li Zuohong, Yang Yingqun, Chen Zhimin, and Wang Ying, *Chin. J. Inorg. Chem.*, 2008, vol. 24, p. 1360.

73. Yang, Y.-Q., Li, C.-H., Li, W., et al., *Chin. J. Struct. Chem.*, 2006, vol. 25, p. 1409.

74. Tabrizi, L., McArdle, P., Ektefan, M., and Chiniforoshan, H., *Inorg. Chim. Acta*, 2016, vol. 439, p. 138.

75. Ge, C., Zhang, X., Yin, J., and Zhang, R., *Chin. J. Chem.*, 2010, vol. 28, p. 2083.

76. Torres, J.F., Bello-Vieda, N.J., Macias, M.A., et al., *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2020, vol. 76, p. 166.

77. Baur, A., Bustin, K.A., Aguilera, E., et al., *Org. Chem. Front.*, 2017, vol. 4, p. 519.

78. Gogoleva, N.V., Shmelev, M.A., Kiskin, M.A., et al., *Russ. Chem. Bull.*, 2016, vol. 65, p. 1198.

Translated by Z. Svitanko