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Influence of the Aromatic Ligand Nature and Synthesis Conditions on the Structures of the Copper Pentafluorobenzoate Complexes

V. V. Kovalev[a], **M. A. Shmelev**[a, *], **G. N. Kuznetsova**[a, †], **V. I. Erakhtina**[b], **G. A. Razgonyaeva**[a], **T. M. Ivanova**[a], **M. A. Kiskin**[a], **A. A. Sidorov**[a], **and I. L. Eremenko**[a]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*
[b] *School no. 1449 named after Hero of the Soviet Union M.V. Vodop'yanov, Moscow, Russia*
**e-mail: shmelevma@yandex.ru*

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Abstract—New pentafluorobenzoate (Pfb) copper complexes with 2,3- and 3,5-lutidine (2,3- and 3,5-Lut, respectively), quinoline (Quin), and 1,10-phenanthroline (Phen) ([$Cu_2(MeCN)_2(Pfb)_4$] (**I**), [Cu(2,3-$Lut)_2(Pfb)_2$] (**II**), [Cu(3,5-$Lut)_4(Pfb)_2$] (**III**), [$Cu(Quin)_2(Pfb)_2$] (**IV**), and [$Cu_2(Phen)_2(Pfb)_4$] (**V**)) are synthesized by the newly developed methods and characterized. The unusual heteroanionic pentafluorobenzoate benzoate (Bnz) ionic compound [$Cu_2(Phen)_2(Pfb)_3]^+(Pnz)^-$ (**VI**) is synthesized. It is shown that the four-bridge binuclear metal cage of complex **I** is not retained in the reactions with various pyridine derivatives. In the case of such α-substituted pyridines as 2,3-lutidine and quinoline, the compositions and structures of the final products of the reactions with copper pentafluorobenzoate are independent of the initial ratio of the reagents and crystallization conditions. It is revealed by the Hirshfeld surface analysis that π···π, C–F···π, C–H···F, and F···F interactions make the major contribution to the stabilization of crystal packings of the synthesized complexes.

Keywords: copper pentafluorobenzoates, heteroanionic complexes, noncovalent interactions, Hirshfeld surface

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INTRODUCTION

Many investigations oriented to the preparation of functional materials are based on the studies of new approaches to the target synthesis of polynuclear coordination compounds of specified compositions and structures [1–5]. The development of new efficient methodologies is a necessary condition for the search for coordination compounds with a required set of physicochemical properties promising for solving various practical problems, including the preparation of new photoactive molecules and related materials [6, 7]. As a rule, a step-by-step change in the composition, geometry of the molecule, and crystal packing of the compounds makes it possible to reveal the influence of a number of factors on the physicochemical properties of new compounds and, thus, to establish structure–property relationships [8–13]. The use of aromatic ligands with donor and acceptor substituents characterized by the formation of strong noncovalent interactions can provide the control of the geometry of the molecules and physicochemical properties due to various intra- and intermolecular noncovalent interactions (C–H···Hal, Hal···Hal, Hal···π, π···π, N–O···π, $NO_2\cdots NO_2$, hydrogen bonds, and others) [14–16]. For example, a combination of the pentafluorobenzoic acid anion with various non-fluorinated aromatic ligands in one molecule can be a convenient and efficient tool for the purposeful formation of compounds with specified molecular and crystal structures [17–22].

Our interest in the copper pentafluorobenzoate complexes is also associated with a diversity of the behavior of the copper compounds depending on the type of the coordination environment [23]. When copper ions exist in the octahedral environment, they can form the same complexes as manganese and cadmium ions do. For instance, copper and manganese form trifluoroacetate coordination polymers $\{M_2(Phen)_2(OOCCF_3)_4\}_n$ [24, 25]. On the one hand, this is possible due to the Jahn–Teller distortion of the coordination polyhedron of the Cu(II) atom and two bonds, whose length can reach 2.6 Å [26]. On the other hand, the copper ion easily transfers to the square environment and forms carboxylate complexes typical of palladium [27–31].

Since the coordination polymers with 2,3-lutidine and isoquinoline were synthesized in the case of cadmium pentafluorobenzoates [32], the formation of

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[†] Deceased.

similar coordination polymers based on a strongly distorted four-bridge fragment could be expected in the case of the octahedral environment of the copper ion. An analysis of available literature data shows that the copper pentafluorobenzoates contain binuclear four-bridge fragments with the "Chinese lantern" structure, but the nonaromatic molecule was coordinated as the neutral axial ligand in these known examples [33, 34]. Copper pentafluorobenzoates with the coordinated pyridine derivatives or other heterocyclic ligands are also known [35–40], but there is no binuclear complex with the "Chinese lantern" structure among them. The four-bridge carboxylate complexes with the "Chinese lantern" structure are most typical of copper and, hence, the situation for the known copper pentafluorobenzoates seems to be very unusual.

Since there are many studies devoted to copper carboxylates, this state of affairs cannot be occasional. The situation will undoubtedly be clarified by the study of the reaction products of copper pentafluorobenzoate with α-substituted pyridines. As known, the use of these ligands provided the formation of the carboxylate complexes with the "Chinese lantern" structure, these complexes were the single reaction products in the predominant part of cases, and even a very significant excess of α-substituted pyridine is of no importance [40].

The purpose of this work is to establish what molecules would be formed in the reactions of copper pentafluorobenzoates with 2,4-lutidine and quinoline. To reveal the presence or absence of a specific role of α-substituted pyridines, it was reasonable to compare the result of the reaction of copper pentafluorobenzoate with 3,5-lutidine as well. As will be shown below, the results of the study turned out to be rather unexpected and, therefore, the scope of the studied copper pentafluorobenzoate complexes was extended, which was finally justified completely.

EXPERIMENTAL

All procedures related to the synthesis of the complexes were carried out in air using MeCN (99%), EtOH (96%), $Cu(NO_3)_2 \cdot 6H_2O$ (reagent grade), $Eu(NO_3)_3 \cdot 5H_2O$ (99.99%, Lankhit), pentafluorobenzoic acid (HPfb, 98%, P&M-Invest), benzoic acid (HBnz, reagent grade), KOH (reagent grade), 2,3-lutidine (2,3-Lut, 98%, Aldrich), 3,5-lutidine (3,5-Lut, 98%, Aldrich), quinoline (Quin, 98%, Sigma-Aldrich), and 1,10-phenanthroline (Phen, 99%, Alfa Aesar). IR spectra were recorded on a Spectrum 65 FT-IR spectrometer (Perkin Elmer) using the attenuated total internal reflectance (ATR) mode in a frequency range of 4000–400 cm^{-1}. Elemental analysis was conducted on a EuroEA-3000 CHNS analyzer (EuroVector).

Synthesis of $[Cu_2(MeCN)_2(Pfb)_4]$ (I). Compound HPfb (1.484 g, 7.000 mmol) was added to a solution of KOH (0.392 g, 7.000 mmol) in methanol (50 mL), and the mixture was stirred at 50°C to the complete dissolution of the starting reactants. Salt $Cu(NO_3)_2 \cdot 6H_2O$ (0.962 g, 3.500 mmol) was added to the resulting solution, and the mixture was stirred at 50°C for 20 min. A precipitate of KNO_3 formed on stirring was filtered off, and the obtained blue solution was evaporated at room temperature to the complete removal of the solvent. The formed blue precipitate was dissolved in acetonitrile (20 mL), and the solution was stored at room temperature with slow evaporation. Blue crystals suitable for X-ray diffraction (XRD) were obtained after 7 days. The crystals of compound **I** were filtered off, washed with cold acetonitrile, and dried in air. The yield of compound **I** was 1.520 g (82.5% based on $Cu(NO_3)_2 \cdot 6H_2O$).

For $C_{32}H_6N_2O_8F_{20}Cu_2$

Anal. calcd., %	C, 36.5	H, 0.6	N, 2.7
Found, %	C, 36.7	H, 0.4	N, 2.9

IR (ATR; ν, cm^{-1}): 3649 w, 3610 w, 3510 w, 2415 w, 1649 s, 1578 s, 1491 s, 1374 s, 1255 w, 1111 m, 992 s, 902 w, 889 m, 758 s, 521 m, 452 m, 428 m, 405 m.

Synthesis of $[Cu(2,3\text{-}Lut)_2(Pfb)_2]$ (II). Compound HPfb (0.300 g, 1.410 mmol) was added to a solution of KOH (0.079 g, 1.410 mmol) in methanol (10 mL), and the mixture was stirred at 50°C until the complete dissolution of the starting reactants. Salt $Cu(NO_3)_2 \cdot 6H_2O$ (0.210 g, 0.705 mmol) was added to the obtained solution, and the mixture was stirred at 50°C for 15 min. A precipitate of KNO_3 formed on stirring was filtered off, and 2,3-lutidine (0.388 mL, 2.820 mmol, Cu : 2,3-Lut = 1 : 4) was added to the resulting blue solution. The obtained solution was stored at room temperature with slow evaporation. Crimson-colored crystals suitable for XRD were formed after 5 days. The crystals of compound **II** were filtered off, washed with cold acetonitrile, and dried in air. The yield of compound **II** was 0.202 g (40.9% based on $Cu(NO_3)_2 \cdot 6H_2O$).

For $C_{28}H_{18}N_2O_4F_{10}Cu$

Anal. calcd., %	C, 48.0	H, 2.6	N, 4.0
Found, %	C, 48.2	H, 2.4	N, 4.3

IR (ATR; ν, cm^{-1}): 3426 w, 3095 w, 2974 w, 2925 w, 2626 w, 2392 w, 1625 s, 1516 s, 1482 s, 1354 s, 1279 s, 1214 m, 1198 m, 1137 m, 1105 m, 989 s, 924 w, 802 m, 754 s, 717 m, 612 m, 585 m, 517 m, 441 w.

Synthesis of $[Cu(3,5\text{-}Lut)_4(Pfb)_2]$ (III) was carried out according to a procedure similar to that for compound **II** using 3,5-lutidine (0.388 mL, 2.820 mmol, Cu : 3,5-Lut = 1 : 4) instead of 2,3-lutidine. We failed to obtain crystals suitable for XRD until the solvent was completely removed. The formed polycrystalline precipitate was repeatedly dissolved in EtOH (8 mL), and the solution was slowly evaporated at room temperature. Blue crystals suitable for XRD were formed after 7 days. The crystals of compound **III** were filtered off, washed with cold water, and dried in air. The of compound **III** was 0.532 g (43.2% based on $Cu(NO_3)_2 \cdot 6H_2O$).

For $C_{42}H_{36}N_4O_4F_{10}Cu$

Anal. calcd., %	C, 51.2	H, 4.0	N, 6.1
Found, %	C, 50.9	H, 4.2	N, 5.9

IR (ATR; ν, cm^{-1}): 3425 w, 3099 w, 2976 w, 2929 w, 2627 w, 2254 w, 1652 s, 1607 s, 1497 s, 1389 s, 1351 s, 1275 m, 1186 m, 1155 m, 1091 s, 986 s, 921 m, 870 m, 829 m, 747 s, 698 s, 582 m, 522 m.

Synthesis of $[Cu(Quin)_2(Pfb)_2]$ (IV). Quinoline (0.024 mL, 0.190 mmol, Cu : Quin = 1 : 1) was added to a solution of complex **I** (0.100 g, 0.095 mmol) in MeCN (10 mL). The resulting solution was stored at room temperature with slow evaporation. Violet crystals suitable for XRD were obtained after 3 days. The crystals of compound **IV** were filtered off, washed with cold acetonitrile, and dried in air. The yield of compound **IV** was 0.023 g (36.2% based on Quin).

For $C_{32}H_{14}N_2O_4F_{10}Cu$

Anal. calcd., %	C, 51.7	H, 1.9	N, 3.7
Found, %	C, 51.8	H, 1.7	N, 3.6

IR (ATR; ν, cm^{-1}): 3459 w, 3091 w, 2997 w, 2325 w, 2254 w, 1907 w, 1618 m, 1511 s, 1485 s, 1365 s, 1318 m, 1284 m, 1232 w, 1134 w, 1104 m, 1052 w, 991 s, 928 m, 808 s, 762 s, 739 m, 703 m, 637 m, 617 m, 584 w, 524 m, 498 m, 463 m.

Synthesis of $[Cu_2(Phen)_2(Pfb)_4]$ (V). Compound HBnz (0.041 g, 0.336 mmol) was added to a solution of KOH (0.019 g, 0.336 mmol) in ethanol (10 mL), and the mixture was stirred at 50°C until the starting compounds dissolved completely. A weighed sample of $Eu(NO_3)_3 \cdot 5H_2O$ (0.048 g, 0.112 mmol) was added to the resulting solution, and the mixture was stirred at 50°C for 15 min. A precipitate of KNO_3 formed on stirring was filtered off, and complex **I** (0.060 g, 0.056 mmol) and 1,10-phenanthroline (0.020 g, 0.112 mmol) were added to the obtained solution. The resulting mixture was stirred at 50°C for 2 h and stored at room temperature with slow evaporation. Blue crystals suitable for XRD were obtained after 6 days. The crystals of compound **V** were filtered off, washed with cold acetonitrile, and dried in air. The yield of compound **V** was 0.016 g (21.3% based on complex **I**).

For $C_{52}H_{16}N_4O_8F_{20}Cu_2$

Anal. calcd., %	C, 46.9	H, 1.2	N, 4.2
Found, %	C, 47.1	H, 1.4	N, 4.3

IR (ATR; ν, cm^{-1}): 3425 w, 3070 w, 2287 w, 1632 m, 1532 s, 1491 s, 1390 s, 1331 m, 1284 m, 1232 w, 1170 m, 1122 m, 1089 w, 990 s, 945 s, 807 m, 760 m, 709 w, 639 m, 619 w, 589 w, 549 w, 490 w, 469 m.

Synthesis of $[Cu_2(Phen)_2(Pfb)_3] \cdot Bnz$ (VI). Compound HBnz (0.041 g, 0.336 mmol) was added to KOH (0.019 g, 0.336 mmol) in ethanol (10 mL), and the solution was stirred at 50°C until the starting reagents dissolved completely. A weighed sample of $Cu(NO_3)_2 \cdot 6H_2O$ (0.050 g, 0.168 mmol) was added to the obtained solution, and the resulting mixture was stirred at 50°C for 15 min. A precipitate of KNO_3 formed on stirring was filtered off, and complex **I** (0.089 g, 0.084 mmol) and 1,10-phenanthroline (0.061 g, 0.336 mmol) were added to the resulting solution. The obtained mixture was stirred at 50°C for 30 min and stored at room temperature with slow evaporation. Blue crystals suitable for XRD were obtained after 10 days. The crystals of compound **VI** were filtered off, washed with cold acetonitrile, and dried in air. The yield of compound **VI** was 0.037 g (35.8% based on complex **I**).

For $C_{52}H_9N_4O_8F_{15}Cu_2$

Anal. calcd., %	C, 50.3	H, 1.7	N, 4.5
Found, %	C, 50.4	H, 1.9	N, 4.4

IR (ATR; ν, cm^{-1}): 3070 m.v.br, 2551 m, 1070 s, 1651 m, 1558 m, 1489 m, 1404 m, 1323 s, 1285 s, 1180 m, 1111 m, 1072 w, 997 s, 931 s, 806 m, 760 m, 712 s, 689 s, 556 m, 543 m, 454 m, 420 m.

XRD of single crystals was carried out on a Bruker Apex II diffractometer equipped with a CCD detector (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) [41]. A semiempirical absorption correction was applied using the SADABS program [42]. The structures were solved by a direct method and refined by least squares first in the isotropic approximation and then in the anisotropic approximation for F^2_{hkl}. The positions of hydrogen atoms were calculated geometrically and refined in the isotropic approximation by the riding model. All calculations were performed using the SHELXL-2018/3 software [43] and Olex2 [44]. In the structure of complex **I**, the pentafluorophenyl fragments are disordered over two positions with the occupancies 0.642/0.358. In the structure of compound **V**, the O(4) oxygen atom of the carboxy group is disordered over two positions with the occupancies 0.72/0.28. The geometries of the metal atom polyhedra were determined using the SHAPE 2.1 program [45]. The crystallographic parameters and structure refinement details for compounds **I**–**VI** are listed in Tables 1 and 2.

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

Parameter	Value		
	I	**II**	**III**
Empirical formula	$C_{32}H_6N_2O_8F_{20}Cu_2$	$C_{28}H_{18}N_2O_4F_{10}Cu$	$C_{42}H_{36}N_4O_4F_{10}Cu$
FW	1053.47	699.98	914.29
T, K	296(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	$P\bar{1}$	$P2_1/n$
a, Å	13.776(3)	7.5374(5)	12.8343(10)
b, Å	17.410(4)	8.8184(7)	9.0410(7)
c, Å	14.837(3)	10.3150(7)	17.6667(14)
α, deg	90	85.157(3)	90
β, deg	91.08(3)	84.742(3)	104.398(3)
γ, deg	90	75.366(3)	90
V, Å^3	3557.8(12)	659.25(8)	1985.6(3)
Z	4	1	2
ρ_{calc}, g/cm^3	1.967	1.763	1.529
μ, mm^{-1}	1.356	0.940	0.646
θ_{max}, deg	25.999	25.995	25.998
Number of measured reflections	8757	5608	11466
Number of independent reflections	3409	2489	3884
Number of reflections with $I > 2\sigma(I)$	2679	2224	3088
R_{int}	0.0565	0.0647	0.0402
Number of refined parameters	3519	3435	3815
GOOF	1.114	1.036	1.027
R_1 ($I > 2\sigma(I)$)	0.0610	0.0467	0.0374
wR_2 ($I > 2\sigma(I)$)	0.1150	0.1190	0.0861
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	–0.713/0.430	–0.961/0.726	–0.405/0.308

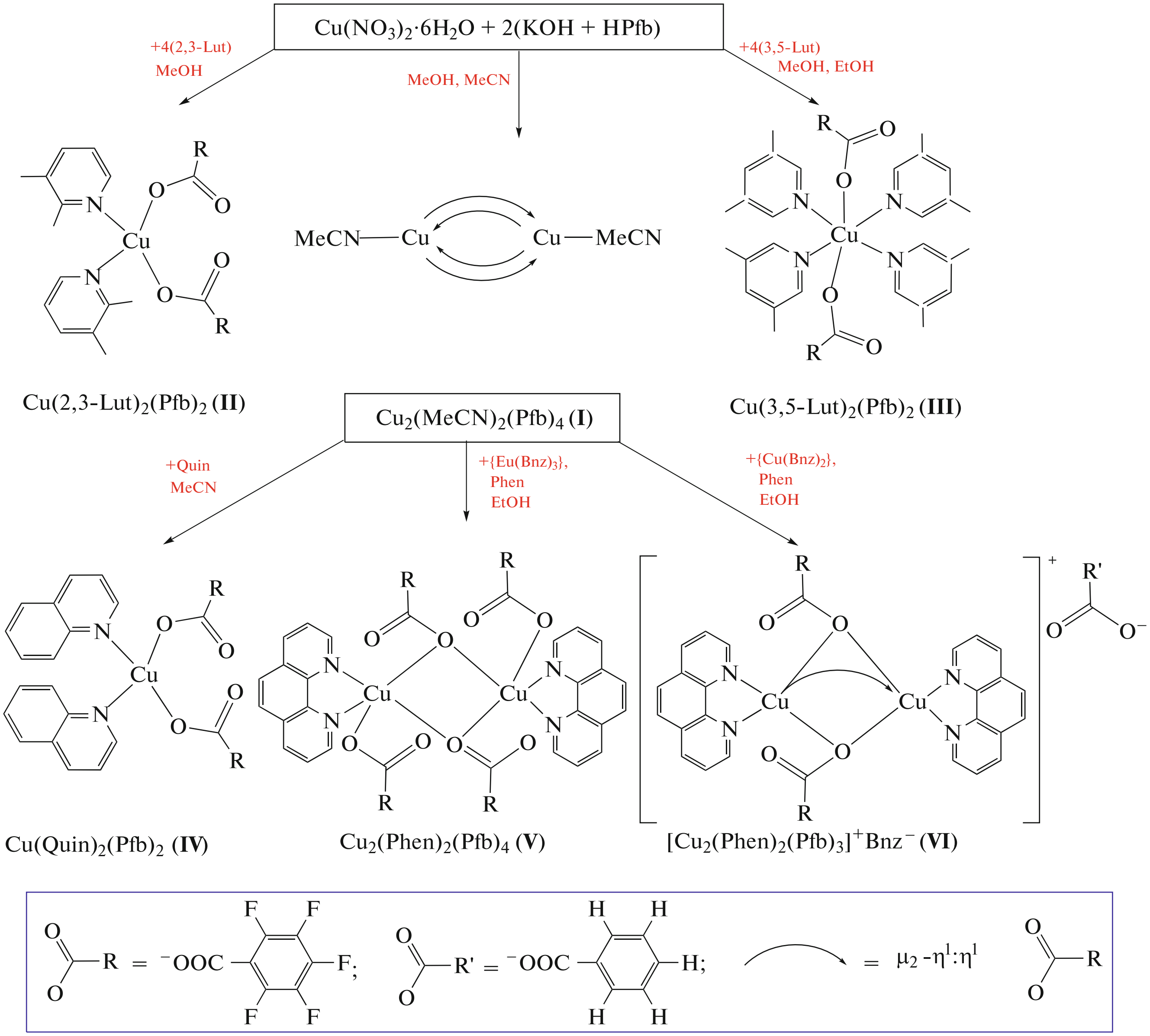
The structural data for compounds **I**–**VI** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2214307 (**I**), 2214304 (**II**), 2214305 (**III**), 2214306 (**IV**), 2218311 (**V**), and 2217785 (**VI**)) and are available at deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif.

In order to evaluate contributions of different noncovalent interactions to the crystal packings of the synthesized complexes, we examined the Hirshfeld surface using the Crystal Explorer 17 program [46, 47].

RESULTS AND DISCUSSION

The reaction of copper nitrate with pentafluorobenzoic acid potassium salt (prepared without isolation by the reaction of potassium hydroxide with pentafluorobenzoic acid) in a methanol–acetonitrile mixture affords crystals of compound $[Cu_2(MeCN)_2(Pfb)_4]$ (**I**, Scheme 1) with the “Chinese lantern” structure typical of the binuclear copper complexes. However, the four-bridge binuclear metal cage of complex **I** was not retained in the reactions with various pyridine derivatives.

The general scheme of the synthesis of complexes **I**–**VI** is shown in Scheme 1.



Scheme 1.

The reaction of copper pentafluorobenzoate with a fourfold 2,3-lutidine or 3,5-lutidine excess resulted in the formation of mononuclear complexes [Cu(2,3-Lut)$_2$(Pfb)$_2$] (**II**, Scheme 1) and [Cu(3,5-Lut)$_4$(Pfb)$_2$] (**III**, Scheme 1). A fourfold excess of 2,3-Lut and 3,5-Lut was used to increase the yield of the expected reaction product, since our previous experience indicated that such an excess allowed the preparation of a single-phase complex in an almost quantitative yield in the case of the compounds with the "Chinese lantern" structure [40].

Taking into account the composition of compound **II**, the Cu to Quin ratio was decreased to 1 : 1 in the reaction of complex **I** with quinoline, and acetonitrile was used as the solvent. This resulted in the formation of compound [Cu(Quin)$_2$(Pfb)$_2$] (**IV**, Scheme 1) analogous to complex **II**; i.e., in the case of such α-substituted pyridines as 2,3-lutidine and quinoline, the compositions and structures of the final reaction products of copper pentafluorobenzoate were the same, although the initial ratio of the reagents and solution composition varied.

Since heterometallic pentabenzoates {Cd$_2$Ln$_2$} and {Zn$_2$Ln$_2$} were described for cadmium and zinc [48–51], it seemed reasonable to synthesize Cu(II)–

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

Parameter	Value		
	IV	**V**	**VI**
Empirical formula	$C_{32}H_{14}CuF_{10}N_2O_4$	$C_{52}H_{16}Cu_2F_{20}N_4O_8$	$C_{52}H_{21}Cu_2F_{15}N_4O_8$
FW	743.99	1331.77	1241.81
T, K	150(2)	296(2)	100(2)
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pnna*
a, Å	7.3250(5)	9.5223(10)	25.0562(19)
b, Å	9.4595(6)	10.6768(12)	13.8791(10)
c, Å	10.3994(6)	12.7802(12)	15.6130(13)
α, deg	84.816(2)	81.280(4)	90
β, deg	82.975(2)	71.143(5)	90
γ, deg	78.030(2)	81.832(5)	90
V, Å^3	698.05(8)	1209.4(2)	5429.5(7)
Z	1	1	4
ρ_{calc}, g/cm^3	1.770	1.829	1.519
μ, mm^{-1}	0.894	1.020	0.890
θ_{max}, deg	30.597	30.509	24.713
Number of measured reflections	7805	15098	36099
Number of independent reflections	4218	7320	4643
Number of reflections with $I > 2\sigma(I)$	3843	5801	3309
R_{int}	0.0166	0.0279	0.1041
Number of refined parameters	4822	856	4137
GOOF	0.936	1.051	1.039
R_1 ($I > 2\sigma(I)$)	0.0305	0.0496	0.0634
wR_2 ($I > 2\sigma(I)$)	0.1151	0.1005	0.1580
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	–0.418/0.428	–0.370/0.330	–1.135/1.053

Ln(III) complexes to obtain a more comprehensive information about copper pentafluorobenzoates. Similar complexes were described earlier for anions of other monocarboxylic acids [52–55]. The result of the synthesis for which we planned to obtain a heterometallic Cu(II)–Ln(III) complex with 1,10-phenanthroline was unexpected, since the homometallic complex $[Cu_2(Phen)_2(Pfb)_4]$ (**V**, Scheme 1), which has previously been detected in the composition of solvate $[Cu_2(Phen)_2(Pfb)_4]\cdot 2HPfb$ [56], was isolated instead of the expected molecular compound $[Cu_2Eu_2(Phen)_2(Pfb)_{10}]$.

The formation of complex **V** shows that heterometallic Cu(II)–Ln(III) pentafluorobenzoate is unstable, most likely, in the system used. It should be mentioned that one of the results of the action of noncovalent interactions of the arene–perfluoroarene type in the systems studied is the destruction of heterometallic fragments, which are highly stable in the most part of other carboxylate anions (pivalate, benzoate, and furoate). For instance, many heterometallic complexes of the $[M_2Li_2L_2(OOCR)_6]$, $[M_2MgL_2(OOCR)_6]$, $[M_2Ln_2L_2(OOCR)_{10}]$, or $[M_2LnL_2(OOCR)_7]$ type (M = Ni(II), Co(II), Cu(II), Zn(II), and Cd(II); L is the monodentate or chelating N-donor ligand) are resistant to the action of a multifold excess of monodentate and chelating pyridine derivatives [57–62]. A similar "destructive" role of aromatic N-donor ligands was observed for cadmium pentafluorobenzoates, where only homometallic cadmium compounds were isolated as a result of attempts to synthesize the complexes with 2,4-lutidine and isoquinoline [32]. We succeeded to synthesize the heterometallic complex $[Cd_2Ln_2(Py)_4(Pfb)_{10}]$ with the monodentate N-donor ligand. However, this complex readily decomposed with a minor pyridine excess to $[Cd(Py)_3(Pfb)_2]$ [32], whereas the stable Cd(II)–Ln(III) compounds were formed by cadmium with 1,10-phenanthroline [51]. In the case of copper, we observed still more "destructive" role of aromatic ligands, which is manifested in the fact that a heterometallic Cu(II)–Ln(III) complex cannot be synthesized even with the chelating ligand, although these compounds are formed in the case of other carboxylate anions [55, 63].

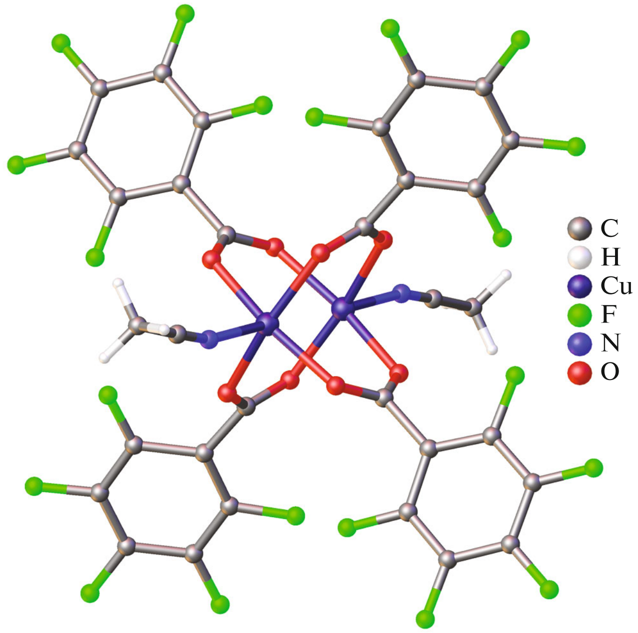


Fig. 1. Structure of complex **I**.

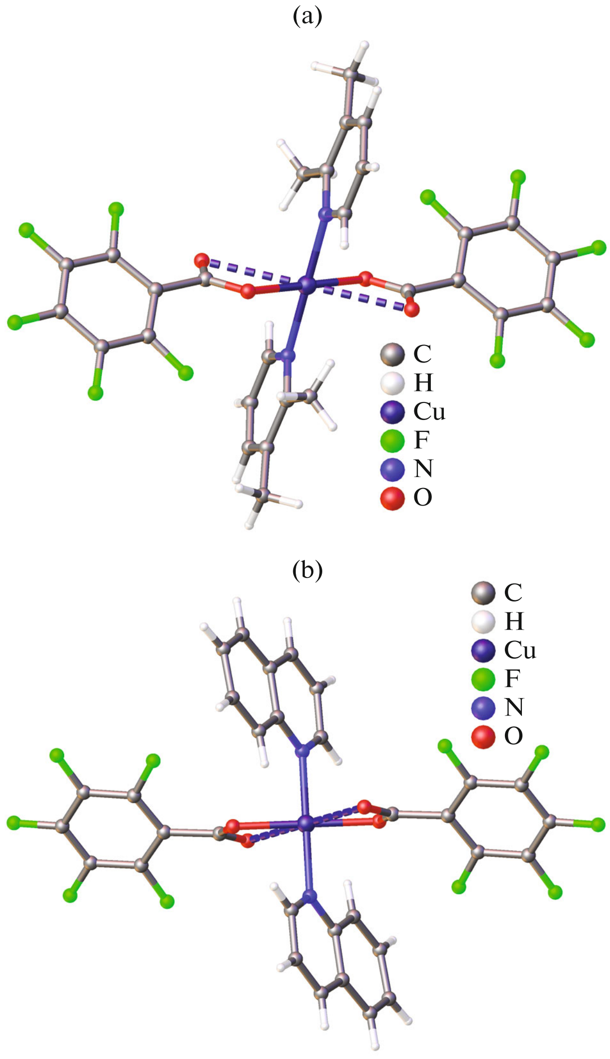


Fig. 2. Structure of complexes (a) **II** and (b) **IV**. The Cu···O contacts are shown by dash.

Such a specific behavior of copper in the pentafluorobenzoate systems shows that it is almost impossible to predict results of the reactions, which were studied in detail for cadmium and zinc and, hence, can be planned surely. This compelled us to reproduce the experiment in which the expected result was not obtained in the case of cadmium. We attempted to synthesize a heteroanionic cadmium compound in which pentafluorobenzoate and benzoate anions would be combined with 1,10-phenanthroline. Instead of this compound, only crystals of the known coordination polymer $\{Cd(Phen)(Pfb)_2\}_n$ were isolated in a high yield [64]. A very unusual heteroanionic $[Cu_2(PhenPfb)_3]^+(Bnz)^-$ compound (**VI**, Scheme 1) was isolated from the reaction of copper benzoate and pentafluorobenzoate with 1,10-phenanthroline in ethanol.

Complex **I** crystallizes in the monoclinic space group *C*2/*c*. Compound **I** consists of two copper cations linked with each other by four μ_2-η^1:η^1-bridging Pfb^- anions (Fig. 1, distance Cu···Cu 2.724(1) Å; Cu–O bond lengths lie in a narrow range of 1.971(4)–1.978(3) Å). Each copper ion additionally coordinates the nitrogen atom of the MeCN molecule (Cu(1)–N(1) 2.147(2) Å). For compound **I**, the Cu–O and Cu–N bond lengths, as well the Cu···Cu distance, lie in the range characteristic of the copper complexes with the “Chinese lantern” structure [65–67]. No significant distortion of the geometry of compound **I** is observed compared to that of the copper benzoate complex $[Cu_2(MeCN)_2(Bnz)_4]$ [68]. The geometry of the CuO_4N coordination polyhedron was analyzed using the Shape2.1 program and corresponds to a tetragonal pyramid (S_q(Cu) = 0.323, copper ion shifts from the O_4 pyramid base by 0.234(2) Å).

The crystal packing of complex **I** exhibits a parallel orientation of the pentafluorobenzoate anions of the adjacent molecules, which possibly indicates the presence of π···π interactions between the aromatic fragments (Table 3). The intermolecular noncovalent interactions C–F···π (Table 4), F···F (Table 5), C–H···F, and C–H···O (Table 6) resulting in the stabilization of the supramolecular cage structure can also be emphasized. It was revealed that the main contribution to the Hirshfeld surface of complex **I** was made by the F···F, H···F, C···F, F···O, and C···C interactions (Table 7).

Complexes **II** and **IV** crystallize in the triclinic space group $P\bar{1}$ with the inversion center on the metal ion and have similar structures. The copper ions in the structures of compounds **II** and **IV** coordinate two

Table 3. Interactions π···π in the crystal packings of complexes **I–VI***

Interaction	Cg···Cg, Å	Symmetry code	Cg···Perp, Å	α, deg
		I		
Pfb···Pfb	3.650(3)	$2 - x, y, 1/2 - z$	3.541(2)	15.9(2)
Pfb···Pfb	3.621(4)	$1 - x, 1 - y, 1 - z$	3.465(3)	0.0(3)
Pfb···Pfb	3.634(8)	$1 - x, 1 - y, 1 - z$	3.465(3)	7.8(6)
Pfb···Pfb	3.756(10)	$1 - x, 1 - y, 1 - z$	3.357(7)	0.0(8)
		II		
2,3-Lut···2,3-Lut	3.7261(18)	$1 - x, y, 1 - z$	3.4135(12)	0.00(14)
Pfb···Pfb	3.5397(18)	$2 - x, 1 - y, - z$	3.2713(13)	0.00(15)
		III		
3,5-Lut···3,5-Lut	3.7173(11)	$1 - x, 2 - y, 1 - z$	3.3475(8)	0.02(10)
		IV		
Pfb···Pfb	3.4921(9)	$-x, 1 - y, 2 - z$	3.3316(6)	0.00(7)
Quin···Quin	3.8262(7)	$1 - x, 1 - y, 2 - z$	3.5040(5)	0.02(4)
		V		
Phen···Pfb	3.5860(16)	$1 - x, 1 - y, 1 - z$	3.3622(11)	7.29(13)
Phen···Phen	3.5726(16)	$1 - x, 2 - y, 1 - z$	3.4509(11)	0.00(13)
		VI		
Phen···Pfb	3.600(3)	$x, 3/2 - y, 3/2 - z$	3.396(2)	2.2(2)
Phen···Phen	3.592(3)	$1 - x, 1 - y, 2 - z$	3.3958(19)	0.2(2)
Bnz···Pfb	3.629(3)	x, y, z	3.4555(19)	3.1(3)
Pfb···Pfb	3.777(3)	$1 - x, 1 - y, 1 - z$	3.497(2)	0.0(3)

* Cg is the centroid of aromatic rings, Perp is the perpendicular to the ring plane, and α is the angle between planes of aromatic fragments.

oxygen atoms of two η^1-Pfb^- anions (Fig. 2, Cu(1)–O(1) 1.970(2) Å for complex **II** and Cu(1)–O(2) 1.969(1) Å for complex **IV**) and two N atoms of two monodentate ligands (Cu(1)–N(1) 1.996(2) Å for complex **II** and Cu(1)–N(1) 2.010(2) Å for complex **IV**) to form the square environment (S_q(Cu) = 0.010 for complex **II**; S_q(Cu) = 0.011 for complex **IV**). The distance between the copper ions and oxygen atoms of the carboxy groups that are not involved in coordination is Cu(1)–O(2) 2.767(2) Å for complex **II** and Cu(1)–O(1) 2.628(1) Å for complex **IV**, which can be considered as a relatively weak interaction [29, 31]. The monodentate coordination mode of the pentafluorobenzoate anion is also confirmed by a significant difference in the C–O bond lengths of the carboxy groups (C(1)–O(1) 1.227(3); C(1)–O(2) 1.270(3) Å for complex **II**; C(1)–O(1) 1.230(2); C(1)–O(2) 1.269(1) Å for complex **IV**) [31]. The dihedral angles between the planes formed by the aromatic fragments of the pentafluorobenzoate anions and N-donor ligands are 87.66(10)° for complex **II** and 88.43(10)° for complex **IV**. The close bond lengths and angles in the structures of compounds **II** and **IV** indicate that the replacement of the 2,3-Lut molecule by Quin exerts no substantial effect on the geometry of the synthesized complexes.

The crystal packings of complexes **II** and **IV** exhibit the formation of π···π interactions between pairs of the N-donor ligand molecules and Pfb anions, whereas no interactions of the arene–perfluoroarene type are observed (Fig. 3, Table 3). According to the Hirshfeld surface analysis, the main contribution to the stabilization of the crystal packing is made by the C···C, C···F, H···F, F···F, and O···H interactions (Tables 4–7), and the replacement of 2,3-lutidine by quinoline in the structure of the complex does not lead to a significant change in the scheme of noncovalent interactions.

The number of the synthesized copper carboxylate compounds with the square environment of the metal center similar to complexes **II** and **IV** is much lower than the number of more typical complexes with the "Chinese lantern" structure. The binuclear compounds with the "Chinese lantern" structure were also synthesized for combinations of a specific carboxylate anion and N-donor ligand capable, as a rule, of form-

Table 4. Interactions C–F···π in the crystal packings of complexes **I**, **II**, and **IV**–**VI***

Interaction	F···Cg, Å	Symmetry code	F···Perp, Å	Angle C–O···Cg, deg
I				
C(11A)–F(11A)···**π**(Pfb)	3.441(7)	x, 1 – y, 1/2 + z	3.328	106.8(5)
C(13A)–F(13A)···**π**(Pfb)	3.211(7)	1 – x, y, 3/2 – z	3.068	104.6(4)
C(14A)–F(14A)···**π**(Pfb)	3.573(10)	1 – x, 1 – y, 1 – z	3.130	69.4(4)
C(11B)–F(11B)···**π**(Pfb)	3.360(9)	x, 1 – y, 1/2 + z	2.994	97.0(8)
C(13B)–F(13B)···**π**(Pfb)	3.492(9)	1 – x, y, 3/2 – z	3.025	115.1(8)
C(14B)–F(14B)···**π**(Pfb)	3.660(16)	1 – x, y, 3/2 – z	3.399	69.2(10)
II				
C(4)–F(4)···π(Pfb)	3.491(2)	2 –x, 1 – y, –z	3.212	69.31(15)
C(5)–F(5)···π(2,3-Lut)	3.171(2)	1 + x, y, –1 + z	3.048	147.79(18)
IV				
C(3)–F(3)···π(Pfb)	3.5189(12)	1 – x, 1 – y, 1 – z	3.312	152.47(8)
C(4)–F(4)···π(Pfb)	3.6652(13)	–x, 1 – y, 2 – z	3.263	65.62(8)
C(5)–F(5)···π(Quin)	3.3138(13)	–1 + x, y, 1 + z	3.174	142.94(10)
V				
C(3)–F(3)···π(Phen)	3.648(2)	2 – x, 1 – y, 1 – z	3.441	19.36
C(6)–F(6)···π(Phen)	3.639(2)	1 – x, 1 – y, 1 – z	3.277	25.77
C(7)–F(7)···π(Phen)	3.4746(19)	1 – x, 1 – y, 1 – z	3.102	26.77
C(10)–F(10)···π(Phen)	3.373(2)	1 – x, 1 – y, 1 – z	3.244	15.90
C(13)–F(13)···π(Pfb)	3.249(2)	2 – x, 1 – y, –z	3.159	13.54
C(14)–F(14)···π(Pfb)	3.635(2)	2 – x, 1 – y, 1 – z	3.209	28.03
VI				
C(4)–F(4)···π(Phen)	3.701(4)	x, 3/2 – y, 3/2 – z	3.376	67.0(3)
C(6)–F(6)···π(Phen)	3.536(5)	x, 3/2 – y, 3/2 – z	3.312	71.5(3)
C(7)–F(7)···π(Phen)	3.484(5)	x, 3/2 – y, 3/2 – z	3.433	91.1(3)
C(10)–F(10)···π(Bnz)	3.773(4)	3/2 – x, 1/2 + y, 3/2 – z	3.411	66.5(3)

* Cg is the centroid of aromatic rings, Perp is the perpendicular to the ring plane, and α is the angle between planes of aromatic fragments.

Table 5. Interactions F···F in the crystal packings of complexes **I**, **IV**, and **VI**

Interaction F···F	*d*, Å	Symmetry code	% of sum of van der Waals radii
I			
F(3)···F(10B)	2.898(11)		98.5
F(5)···F(10B)	2.711(12)	x, 1 – y, –1/2 + z	92.2
F(6)···F(11B)	2.879(9)	3/2 – x, 1/2 + y, 1/2 – z	97.9
F(6)···F(14A)	2.894(8)	1/2 + x, 3/2 – y, –1/2 + z	98.4
F(7)···F(14A)	2.702(8)	1/2 + x, 3/2 – y, –1/2 + z	91.9
IV			
F(4)···F(5)	2.880(2)	2 – x, 2 – y, 1 – z	97.9
V			
F(3)···F(4)	2.930(3)	1 – x, 1 – y, 2 – z	98.6
VI			
F(6)···F(11)	2.738(5)	–1/2 + x, 3/2 – y, –1/2 + z	93.1
F(5)···F(5)	2.828(4)	x, 3/2 – y, 3/2 – z	95.9
F(12)···F(11)	2.719(4)	x, 3/2 – y, 3/2 – z	92.2

Table 6. Interactions C–H···F and C–H···O in the crystal packings of complexes **I** and **III–VI**

D–H···A	Distance, Å D–H	Distance, Å H···A	Distance, Å D···A	Symmetry code	Angle D–H···A, deg
I					
C(10)–H(10)···F(7)	0.95	2.49	3.280(4)	$1 - x, -y, 1 - z$	141
C(11)–H(11)···O(2)	0.95	2.49	3.193(4)	$1 + x, y, z$	130
C(13)–H(13*C*)···F(3)	0.98	2.49	3.305(4)	$1 - x, 1 - y, 1 - z$	141
III					
C(8)–H(8)···O(1)	0.95	2.25	2.974(3)		152
C(12)–H(12)···O(1)	0.95	2.41	3.142(3)	$1 - x, 1 - y, 1 - z$	159
C(14)–H(14*C*)···F(5)	0.95	2.53	3.494(3)	$3/2 - x, -1/2 + y, 3/2 - z$	173
C(15)–H(15)···O(1)	0.95	2.43	3.038(3)		158
C(19)–H(19)···O(2)	0.95	2.30	3.204(3)	$1 - x, 1 - y, 1 - z$	144
IV					
C(9)–H(9)···O(1)	0.95	2.42	3.175(5)	$1 + x, y, z$	136
C(15)–H(15)···F(4)	0.95	2.55	3.254(2)	$x, 1 + y, -1 + z$	131
V					
C(25)–H(25)···O(2)	0.93	2.39	3.192(3)	$1 - x, 2 - y, 1 - z$	144
C(26)–H(26)···O(4B)	0.93	2.38	3.238(10)	$1 - x, 2 - y, 1 - z$	152
VI					
C(5S)–H(5*S*)···F(3)	0.95	2.49	3.236(10)		135
C(13)–H(13)···F(10)	0.95	2.39	3.232(6)		148
C(17)–H(17)···F(5)	0.95	2.40	3.153(6)	$x, y, 1 + z$	136

Table 7. Contribution of noncovalent interactions to the total Hirshfeld surface of complexes **I–VI**

Interaction	Compound					
	I	**II**	**III**	**IV**	**V**	**VI**
	%					
C···C	7.1	5.0	2.1	8.3	8.3	10.8
C···F	18.3	14.7	6.6	14.6	7.8	2.8
H···F	23.0	35.7	33.4	36.7	40.4	32.7
F···F	27.9	6.7	2.1	6.0	17.2	11.0
O···F	10.5	3.8	2.0	4.5	4.1	3.0
O···H	3.9	8.4	1.9	6.2	8.8	11.3

ing mononuclear complexes of the discussed type. For instance, monochloroacetate with 2-methylpyridine $[Cu(L)_2(OOCR)_2]$ [69] and binuclear complex $[Cu_2(L)_2(\mu\text{-}OOCR)_4]$ [70] are known. The same situation is observed for the benzoate complexes with 2-aminopyridine [71], and benzoates form binuclear $[Cu_2(L)_2(\mu\text{-}OOCR)_4]$ complexes with other aromatic N-donor ligands as well [67, 72, 73].

Complex **III** crystallizes in the monoclinic space group $P2_1/n$ with the inversion center on the metal ion. The octahedral environment of the copper ions in the structure of complex **III** is formed due to two oxygen atoms of the η^1-Pfb^- anions and four nitrogen atoms of four 3,5-Lut molecules (Fig. 4, $S_q(Cu)$ = 0.946). An insignificant distortion of the metal ion polyhedron is also confirmed by the bond angles

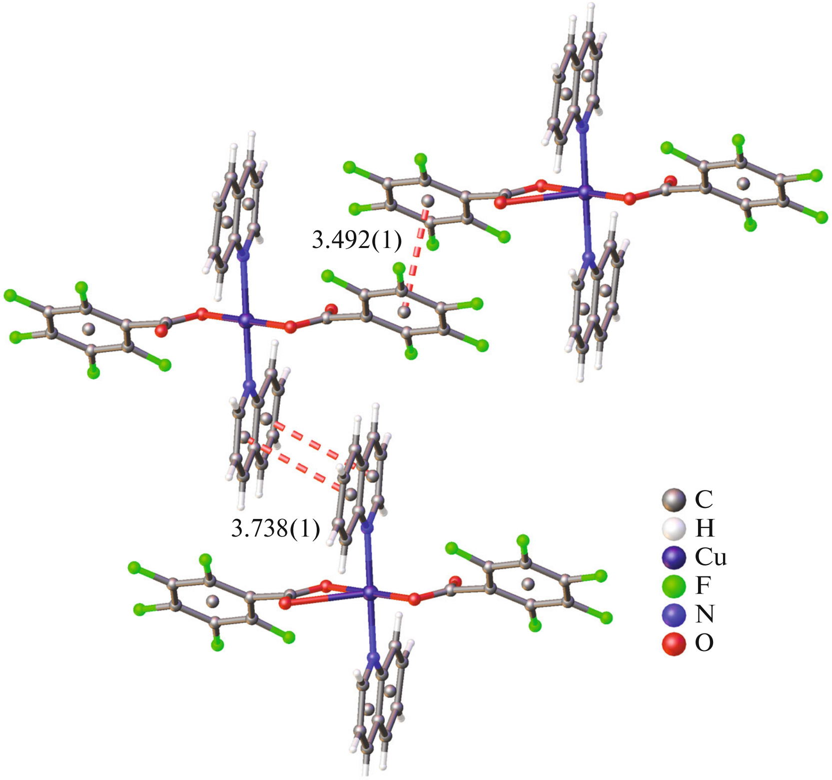


Fig. 3. Fragment of the crystal packing of complex **IV**. The aromatic cycles between which π···π interactions occur are shown by dash.

N(1)Cu(1)N(2) (89.90(7)°) and N(1)Cu(1)O(1) (92.49(6)°). The Cu–N distances (2.060(2) and 2.030(2) Å) in complex **III** are typical of Cu–N bonds, whereas the Cu(1)–O(1) bond considerably elongates (2.483(4) Å). The O(2) atoms are not involved in the coordination to the copper ions, and the Cu(1)···O(2) distance is 4.155(2) Å.

As in the case of complexes **II** and **IV**, the crystal packing of compound **III** contains no interactions of the arene–perfluoroarene type, whereas pairs of 3,5-Lut molecules form π···π interactions (Table 3). The intermolecular noncovalent C–H···F and C–H···O interactions also contribute to the stabilization of the crystal packing (Table 6) and result in the stabilization of the supramolecular cage structure. According to the Hirshfeld surface analysis, the main contribution to the crystal packing stabilization is made by the C···F and H···F interactions (Table 7), whereas the contribution of the C···C, F···F, and O···H interactions decreases significantly compared to that for complexes **II** and **IV**.

According an analysis of the Cambridge Structural Database (CSD), only several examples of the copper complexes with the composition $[Cu(RCOO)_2(L)_4]$, where RCOO is the carboxylic acid anion, and L is the monodentate N-donor ligand, are described [74–80]. An insignificant number of the complexes with 3*d*-metal ions similar to complex **III** was described, and the most part of them was synthesized using the crystallization of anhydrous carboxylates from a pyridine solution [74, 81–87]. An inert atmosphere and the absence of water were necessary for the synthesis of iron pivalate and acetate $[Fe(Py)_4(OOCR)_2]$ [84, 85], whereas these conditions were possibly needless for

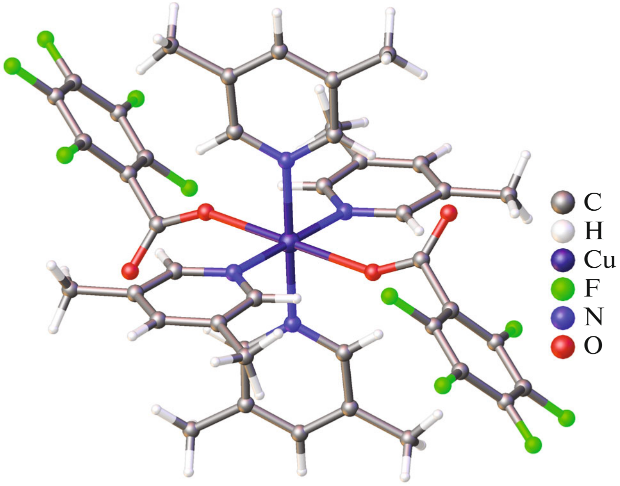


Fig. 4. Structure of complex **III**.

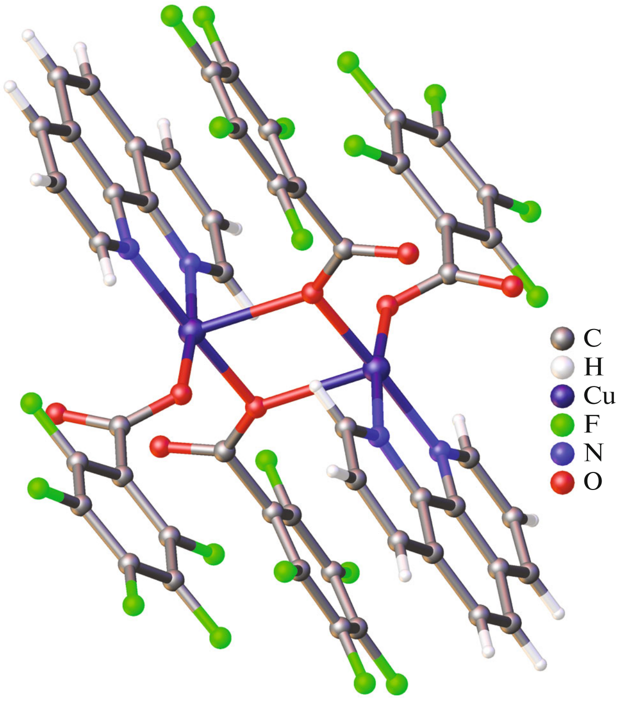


Fig. 5. Structure of complex **V**.

manganese [88], copper [79], and cobalt [87] trifluoroacetates. Probably, complexes of the [M(Py)$_4$(OOCR)$_2$] type with anions of strong carboxylic acids will be formed in many other cases as well.

Complex **V** crystallizes in the triclinic space group $P\bar{1}$ with the inversion center between two copper ions. In the structure of complex **V**, the metal ions are linked with each other via two η^1-Pfb$^-$ anions with the formation of the binuclear metallic cage (Fig. 5, Cu(1)–O(1) 1.968(2), Cu···Cu 3.3681(3) Å, angle Cu(1)O(1)Cu(1) 100.81(8)°). Each metal ion builds up its environment to a square pyramid due to the coordination of the Pfb$^-$ anion and chelate-bound Phen molecule (Cu(1)–O(3) 1.939(1), Cu(1)–N(1) 2.018(2), Cu(1)–N(2) 2.026(2) Å, S_q(Cu) = 1.667). The O(2) and O(4) atoms are not involved in the coordination to the copper ions, and the Cu(1)···O(2) and Cu(1)···O(4) distances are 2.997(4) and 3.084(2) Å, respectively, which exceed the sums of the van der Waals radii.

The aromatic fragments of the Pfb$^-$ anions in the crystal packing of compound **V** are involved in the formation of π···π interactions of the arene–perfluoroarene type with the 1,10-Phen molecules to form a supramolecular chain directed along the *a* axis (Fig. 6, Table 3). The crystal packing is also stabilized by the F···F, C–F···π, and C–H···O interactions (Tables 4–6) with the formation of a layered supramolecular structure. According to the Hirshfeld surface analysis, the main contribution to the crystal structure stabilization is made by the H···F, F···F, O···H, and C···C interactions (Table 7).

The binuclear copper complexes with the structure similar to that of compound **V** were earlier synthesized for a series of mono- [56, 89–97] and dicarboxylic acids [93, 98–101]. The binuclear copper pentafluorobenzoate complexes similar to complex **V** with solvate molecules of pentafluorobenzoic acid ([Cu$_2$(Phen)$_2$(Pfb)$_4$]·2HPfb [56]) and with 2,2'-bipyridyl (Bpy) as the N-donor ligand ([Cu$_2$(Bpy)$_2$(Pfb)$_4$] [94]) were also synthesized. The replacement of Bpy by Phen in the structure of the binuclear copper pentafluorobenzoate complex does not result in a significant change in the geometry of the molecule, but an approach of the aromatic cycles of the pentafluorobenzoate anions and N-donor ligand molecules by ~0.3 Å is observed, which possibly indicates the enhancement of noncovalent interactions of the arene–perfluoroarene type. The introduction of a solvate acid molecule results in the formation of additional π···π interactions between the aromatic anions and solvate molecules of the acid, which exerts no substantial effect on the geometry of the binuclear molecule.

A specific feature of complex **V** is that its structure is nearly the same as the structure of the binuclear fragment of the {Cd(Phen)(Pfb)$_2$}$_n$ coordination polymer [64]. However, although the structure of compound **V** is preorganized for polymerization, its molecule is very stable owing to the coordination saturation of the copper atom. Stacking interactions between the

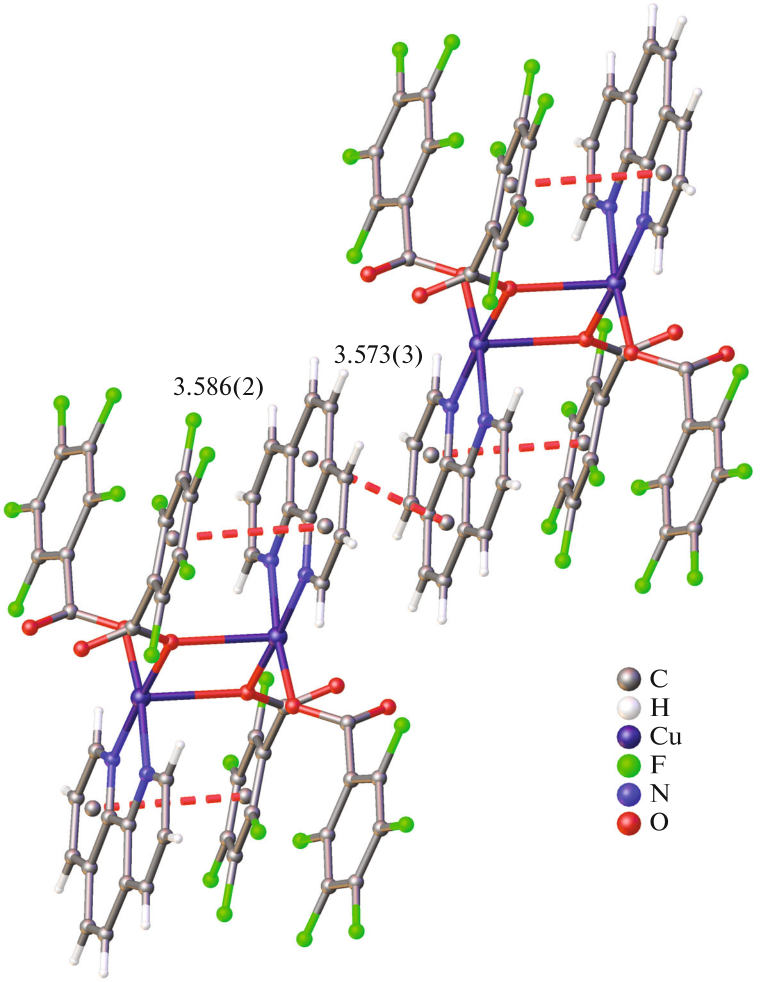


Fig. 6. Fragment of the crystal packing of complex **V**. The aromatic cycles between which π···π interactions occur are shown by dash.

Phen molecules and pentafluorophenyl substituents of the carboxylate anions are observed in both the $\{Cd(Phen)(Pfb)_2\}_n$ coordination polymer and binuclear complex **V**. Owing to this, the aromatic fragments are oriented in parallel and form an "oblate" structure. If the binuclear fragment is "cut" from the $\{Cd(Phen)(Pfb)_2\}_n$ coordination polymer, this fragment would contain unblocked coordinatively unsaturated metal centers. Under the real conditions, this structure can be stable only due to the coordination of additional ligands, as it took place for the formation of unusual binuclear 2,3,4,5-tetrafluorobenzoate complexes $[Cd_2(H_2O)_2(Phen)_2(OOCC_6F_4H)_4]$ and $[Cd_2(H_2O)_2(Quin)_2(OOCC_6F_4H)_4]$ [64].

Complex **VI** crystallizes in the orthorhombic space group *Pnna*. Compound **VI** consists of the binuclear $[Cu_2(Pfb)_3(Phen)_2]^+$ cation and outer-sphere anion of benzoic acid. In the binuclear cation, two copper ions are bound to each other via one μ_2-η^1:η^1 Pfb^- and two η^1-Pfb^- anions (Fig. 7; Cu(1)–O(1) 2.324(3), Cu(1A)–O(1A) 1.951(3), Cu(1)–O(3) 1.942(3), and Cu···Cu 3.237(1) Å). Each copper anion builds up its environment to a tetragonal pyramid due to the coordination of two nitrogen atoms of the Phen molecule (Cu(1)–N(2) 1.991(4), Cu(1)–N(1) 2.003(5) Å; S_q(Cu) = 2.482). The O(2) atom is not involved in the coordination to the copper ions, and the Cu(1)···O(2) distance is 2.991(4) Å.

Compound **VI** is unusual, because anions of a stronger carboxylic acid are coordinated and an anion of a much weaker acid becomes the outer-sphere anion (pK_a(HBnz) = 4.20, pK_a(HPfb) = 1.48). As a rule, benzoate anions in the carboxylate systems cannot be outer-sphere, whereas this function is rather usual for anions of strong carboxylic acids [102–104]. Some three-bridge cationic copper complexes with monocarboxylic acid anions similar to compound **VI** are known [105–110], but the stronger acid anions were counterions in all known examples.

All aromatic fragments in compound **VI** are involved in the π···π interactions (Fig. 8). The struc-

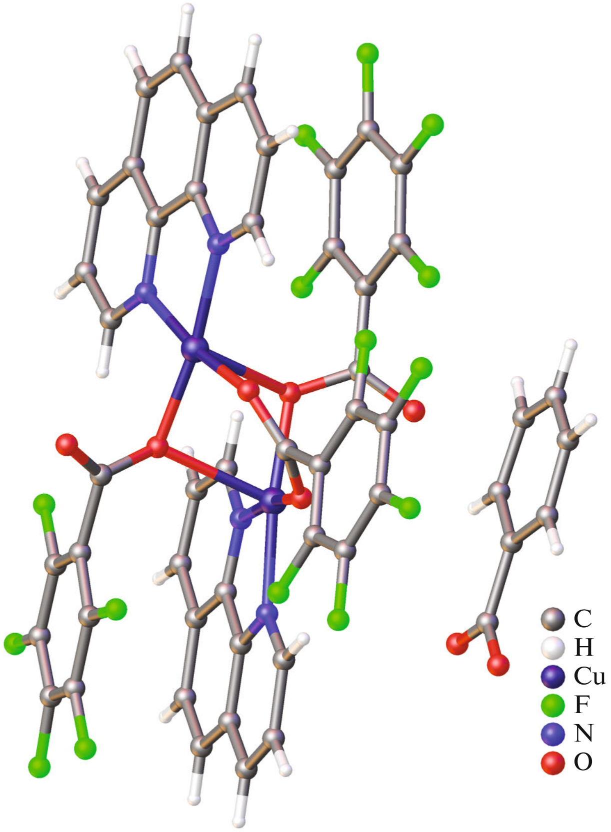


Fig. 7. Structure of compound **VI**.

ture of the binuclear cation exhibits stacking interactions between the coordinated 1,10-phenanthroline molecules and pentafluorophenyl substituents of the anions (Table 3). One pentafluorobenzoate anion is not involved in the intramolecular stacking but participates in the π···π interactions with the outer-sphere anion of benzoic acid, which results in the formation of supramolecular chains directed along the *b* axis. The crystal packing of complex **VI** is also stabilized by a series of C–F···π, C–H···F, and F···F interactions (Tables 4–6). The main contribution to the Hirshfeld surface is made by the H···F, F···F, O···H, and C···C interactions. We can also mention an increase in the role of the O···H and C···C interactions and a significant decrease in the role of the H···F and F···F interactions upon the introduction of the benzoate anion into the structure of heteroanionic complex **VI** compared to pentafluorobenzoate complex **V** (Table 7).

Thus, we showed that the substitution of coordinated acetonitrile molecules in complex **I** by aromatic heterocyclic N-donor ligands led to the destruction of the binuclear metal cage and formation of different mononuclear compounds. Probably, since in the systems considered the copper atom forms no octahedral environment, no analogs of the cadmium pentafluorobenzoate coordination polymers with heterocyclic monodentate N-donor ligands were prepared. The stability of the $[Cu_2(Phen)_2(Pfb)_4]$ binuclear complex is determined by the tetragonal pyramidal environment of the copper atoms that are coordinatively saturated in this complex. It is shown for the heteroanionic copper benzoate pentafluorobenzoate complex that the introduction of the aromatic anion of the second type results in the stabilization of the untypical ionic compound in which the anion of a weaker acid acts as the outer-sphere counterion.

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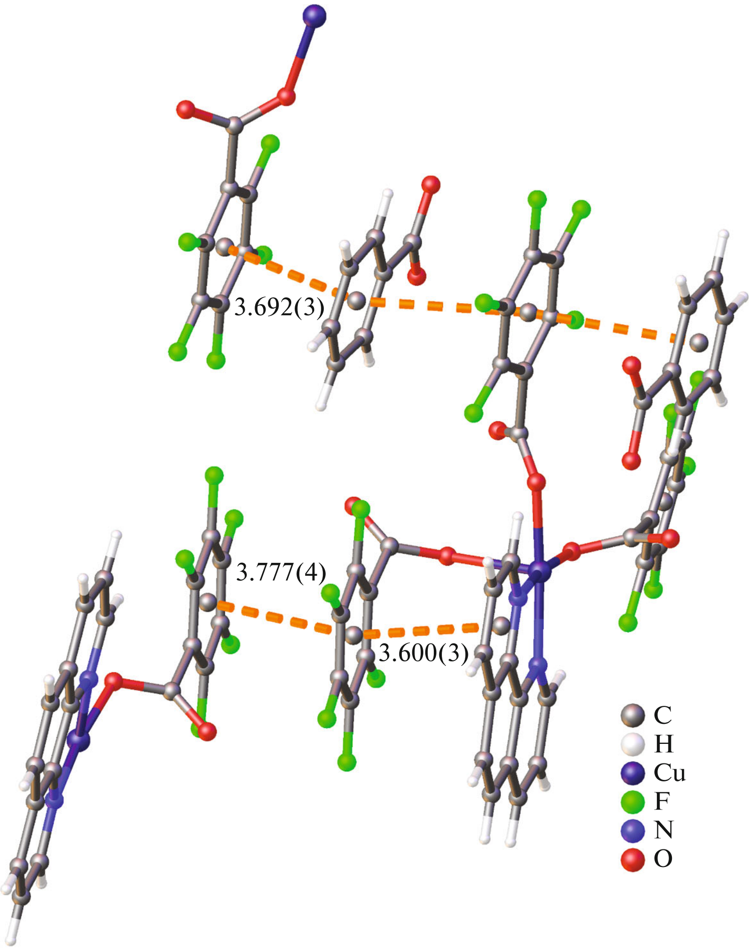

Fig. 8. Scheme of intermolecular contacts in the supramolecular chain of compound **VI**. The aromatic cycles between which π···π interactions occur are shown by dash.

FUNDING

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Zhang, Z. and Zaworotko, M.J., *Chem. Soc. Rev.*, 2014, vol. 43, p. 5444.
2. Bradberry, S.J., Savyasachi, A.J., Martinez-Calvo, M., and Gunnlaugsson, T., *Coord. Chem. Rev.*, 2014, vols. 273–274, p. 226.
3. Chen, D.-M., Zhang, N.-N., Liu, C.-S., and Du, M., *J. Mater. Chem.*, 2017, vol. 5, p. 2311.
4. Kohnke, F.H., Mathias, J.P., and Fraser-Stoddart, J., *Angew. Chem.*, 1989, vol. 28, no. 8, p. 1103.
5. Bazhina, E.S., Bovkunova, A.A., Shmelev, M.A., et al., *Polyhedron*, 2022, vol. 228, p. 116174.
6. Barry, D.E., Caffreya, D.F., and Gunnlaugsson, T., *Chem. Soc. Rev.*, 2016, vol. 45, p. 3244.
7. Su, J., Yuan, S., Cheng, Y.-X., et al., *Chem. Sci.*, 2021, vol. 12, p. 14254.
8. Shmelev, M.A., Kuznetsova, G.N., Gogoleva, N.V., et al., *Russ. Chem. Bull.*, 2021, vol. 7, no. 5, p. 830.
9. Bondarenko, M.A., Novikov, A.S., Sokolov, M.N., and Adonin, S.A., *Organics*, 2022, vol. 10, no. 10, p. 151.
10. Adonin, S.A., Bondarenko, M.A., Novikov, A.S., et al., *Crystals*, 2020, vol. 10, p. 289.
11. Shmelev, M.A., Chistyakov, A.S., Razgonyaeva, G.A., et al., *Crystals*, 2022, vol. 12, p. 508.
12. Zhou, W.-L., Chen, Y., Lin, W., and Liu, Y., *Chem. Commun.*, 2021, vol. 57, p. 11443.
13. Koshevoy, I.O., Krause, M., and Klein, A., *Coord. Chem. Rev.*, 2020, vol. 405, p. 213094.
14. Adonin, S.A., Novikov, A.S., Sokolov, M.N., and Fedin, V.P., *Russ. J. Coord. Chem.*, 2020, vol. 46, p. 302.
15. Adonin, S.A., Novikov, A.S., and Fedin, V.P., *Russ. J. Coord. Chem.*, 2020, vol. 46, p. 37.

16. Shmelev, M.A., Voronina, J.K., Evtyukhin, M.A., et al., *Inorganics*, 2022, vol. 10, no. 11, p. 194.
17. Sharma, R.P., Saini, A., Kumar, S., et al., *J. Mol. Struct.*, 2017, vol. 1128, p. 135.
18. Shmelev, M.A., Voronina, Yu.K., Chekurova, S.S., et al., *Russ. J. Coord. Chem.*, 2021, vol. 47, p. 551.
19. Kong, Y.-J., Han, L.-J., Fan, L.-T., et al., *J. Fluorine Chem.*, 2016, vol. 186, p. 40.
20. Han, L.-J. and Kong, Y.-J., *Z. Anorg. Allg. Chem.*, 2014, vol. 640, no. 10, p. 2007.
21. Shmelev, M.A., Voronina, Yu.K., Gogoleva, N.V., et al., *Russ. J. Coord. Chem.*, 2022, vol. 48, no. 4, p. 224.
22. Malkerova, I.P., Kayumova, D.B., Belova, E.V., et al., *Russ. J. Coord. Chem.*, 2022, vol. 48, no. 10, p. 608.
23. Pinto, C.B., Dos Santos, L.H.R., and Rodrigues, B.L., *J. Appl. Crystallogr.*, 2020, vol. 53, p. 1321.
24. Sen, S., Saha, M.K., Gupta, T., et al., *J. Chem. Crystallogr.*, 1998, vol. 28, p. 771.
25. Andruh, M., Roesky, H.W., Noltemeyer, M., and Schmidt, H.-G., *Polyhedron*, 1993, vol. 12, no. 23, p. 2901.
26. Harding, M.M., *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2000, vol. 56, p. 857.
27. Bondarenko, M.A., Abramov, P.A., Novikov, A.S., et al., *Polyhedron*, 2022, vol. 214, p. 15644.
28. Li, Z., Yuan, Y., Zhang, Y., et al., *Z. Anorg. Allg. Chem.*, 2017, vol. 643, no. 10, p. 647.
29. Sanchez-Sala, M., Pons, J., Alvarez-Larena, A., et al., *ChemistrySelect*, 2017, vol. 2, no. 35, p. 11574.
30. Obaleye, J.A., Ajibola, A.A., Bernardus, V.B., and Hosten, E.C., *J. Mol. Struct.*, 2020, vol. 1203, p. 127435.
31. Rajakannu, P., Kaleeswaran, D., Banerjee, S., et al., *Inorg. Chim. Acta*, 2019, vol. 486, p. 283.
32. Shmelev, M.A., Gogoleva, N.V., Kuznetsova, G.N., et al., *Russ. J. Coord. Chem.*, 2020, vol. 46, no. 8, p. 557.
33. Larionov, S.V., Glinskaya, L.A., Klevtsova, R.F., et al., *Z. Neorg. Khim.*, 1991, vol. 36, p. 2514.
34. Han, L.-J., Kong, Y.-J., and Huang, M.-M., *Inorg. Chim. Acta*, 2020, vol. 514, p. 120019.
35. Hashim, I.I., Scattolin, T., Tzouras, N.V., et al., *Dalton Trans.*, 2022, vol. 51, p. 231.
36. Makoto, H., Yoshiyuki, I., Taku, Y., et al., *Bull. Chem. Soc. Jpn.*, 2009, vol. 82, no. 10, p. 1277.
37. Han, L.-J. and Kong, Y.-J., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2014, vol. 70, no. 11, p. 1017.
38. Sharma, R.P., Saini, A., Singh, S., et al., *J. Fluorine Chem.*, 2010, vol. 131, no. 4, p. 456.
39. Ge, C., Zhang, X., Yu, F., et al., *J. Chem. Crystallogr.*, 2008, vol. 38, p. 501.
40. Kuznetsova, G.N., Nikolaevskii, S.A., Yambulatov, D.S., et al., *J. Struct. Chem.*, 2021, vol. 62, no. 2, p. 184.
41. *SMART (control) and SAINT (integration). Software. Version 5.0*, Madison: Bruker AXS Inc., 1997.
42. Krause, L., Herbst-Irmer, R., Sheldrick, G.M., and Stalke, D., *J. Appl. Crystallogr.*, 2015, vol. 48, p. 3.
43. Spek, A.L., *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2009, vol. 65, no. 2, p. 148.
44. Dolomanov, O.V., Bourhis, L.J., Gildea, R., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339.
45. Casanova, D., Llunell, M., Alemany, P., and Alvarez, S., *Chem.-Eur. J.*, 2005, vol. 11, p. 1479.
46. Spackman, P.R., Turner, M.J., McKinnon, J.J., et al., *J. Appl. Crystallogr.*, 2021, vol. 54, p. 1006.
47. Edwards, A.J., Mackenzie, C.F., Spackman, P.R., et al., *Faraday Discuss.*, 2017, vol. 203, p. 93.
48. Shmelev, M.A., Gogoleva, N.V., Ivanov, V.K., et al., *Russ. J. Coord. Chem.*, 2022, vol. 48, no. 9, p. 539.
49. Shmelev, M.A., Polunin, R.A., Gogoleva, N.V., et al., *Molecules*, 2021, vol. 26, no. 14, p. 4296.
50. Belousov, Y.A., Kiskin, M.A., Sidoruk, A.V., et al., *Aust. J. Chem.*, 2022, vol. 75, no. 9, p. 572.
51. Shmelev, M.A., Kiskin, M.A., Voronina, J.K., et al., *Materials*, 2020, vol. 13, no. 24, p. 5689.
52. Sidorov, A.A., Gogoleva, N.V., Bazhina, E.S., et al., *Pure Appl. Chem.*, 2020, vol. 92, no. 7, p. 1093.
53. Bovkunova, A.A., Bazhina, E., Evstifeev, I.S., et al., *Dalton Trans.*, 2021, vol. 50, p. 12275.
54. Pushikhina, O.S., Kozlyakova, E.S., Karpova, E.V., and Tafeenko, V.A., *Z. Anorg. Allg. Chem.*, 2021, vol. 647, no. 22, p. 2023.
55. Li, Y., Zhang, C., Yu, J.-W., et al., *Inorg. Chim. Acta*, 2016, vol. 445, p. 110.
56. Ge, C., Zhang, X., Yin, J., and Zhang, R., *Chin. J. Chem.*, 2010, vol. 28, no. 10, p. 2083.
57. Shmelev, M.A., Gogoleva, N.V., Sidorov, A.A., et al., *Inorg. Chim. Acta*, 2021, vol. 515, p. 120050.
58. Shmelev, M.A., Gogoleva, N.V., Sidorov, A.A., et al., *ChemSelect*, 2020, vol. 5, no. 28, p. 8475.
59. Shmelev, M.A., Voronina, Yu.K., Gogoleva, N.V., et al., *Russ. Chem. Bull.*, 2020, vol. 69, p. 1544.
60. Melnikov, S.N., Evstifeev, I.S., Nikolaveskii, S.A., et al., *New J. Chem.*, 2021, vol. 45, p. 13349.
61. Nikolaevskii, S.A., Petrov, P.A., Sukhikh, T.S., et al., *Inorg. Chim. Acta*, 2020, vol. 508, p. 119643.
62. Gogoleva, N.V., Kuznetsova, G.N., Shmelev, M.A., et al., *J. Solid State Chem.*, 2021, vol. 294, p. 121842.
63. Wu, B., Lu, W., and Zheng, X., *Transition Met. Chem.*, 2003, vol. 28, p. 323.
64. Shmelev, M.A., Kuznetsova, G.N., Dolgushin, F.M., et al., *Russ. J. Coord. Chem.*, 2021, vol. 47, p. 127.
65. Yambulatov, D.S., Nikolaevskii, S.A., Lutsenko, I.A., et al., *Russ. J. Coord. Chem.*, 2020, vol. 46, p. 772.
66. Zeng, Z., Cai, J., Li, F., et al., *RSC Adv.*, 2021, vol. 11, p. 40040.
67. Sharma, P., Dutta, D., Gomila, R.M., et al., *Polyhedron*, 2021, vol. 208, p. 115409.
68. Lah, N., Giester, G., Segedin, P., Murn, A., et al., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.,* 2001, vol. 57, p. 546.
69. Davey, G. and Stephens, F.S., *J. Chem. Soc. A*, 1971, p. 1917.
70. Davey, G. and Stephens, F.S., *J. Chem. Soc. A*, 1970, p. 2803.
71. Kozlevcar, B., Lah, N., Zlindra, D., et al., *Acta Chim. Slov.*, 2001, vol. 48, p. 363.

72. Kozlevcar, B., Murn, A., Podlipnik, K., et al., *Croat. Chem. Acta*, 2004, vol. 77, p. 613.
73. Buijs, W., Comba, P., Corneli, D., et al., *Eur. J. Inorg. Chem.*, 2001, p. 3143.
74. Li, L.-M., Guo, H.-M., and Li, Y.-F., *Z. Krist New, Cryst. Struct.*, 2012, vol. 227, p. 257.
75. Dickie, D.A., Schatte, G., Jennings, M.C., et al., *Inorg. Chem.*, 2006, vol. 45, no. 4, p. 1646.
76. Pradilla, S.J., Chen, H.W., Koknat, F.W., and Fackler, J.P., Jr., *Inorg. Chem.*, 1979, vol. 18, no. 12, p. 3519.
77. Gajewska, M.J., Ching, W.-M., Wen, Y.-S., and Hung, C.-H., *Dalton Trans.*, 2014, vol. 43, p. 14726.
78. Ghosh, S.K. and Bharadwaj, P.K., *Inorg. Chem.*, 2004, vol. 43, no. 22, p. 6887.
79. Pretorius, J.A. and Boeyens, J.C.A., *J. Inorg. Nucl. Chem.*, 1978, vol. 40, no. 10, p. 1745.
80. Baruah, J.B., Singh, W., and Karmakar, A., *J. Mol. Struct.*, 2008, vol. 892, nos. 1–3, p. 84.
81. Neary, M.C. and Parkin, G., *Polyhedron*, 2016, vol. 116, p. 189.
82. Edema, J.J.H., Hao, S., Gambarotta, S., and Bensimon, C., *Inorg. Chem.*, 1991, vol. 30, no. 12, p. 2584.
83. Li, L.-M., Jian, F.-F., and Ren, X.-Y., *Acta Crystrallog., Sect. E: Struct. Rep. Online*, 2009, vol. 65, p. m1041.
84. Çelenligil-Çetin, R., Staples, R.J., and Stavropoulos, P., *Inorg. Chem.*, 2000, vol. 39, no. 25, p. 5838.
85. Singh, B., Long, J.R., Papaefthymiou, G.C., and Stavropoulos, P., *J. Am. Chem. Soc.*, 1996, vol. 118, no. 24, p. 5824.
86. Tapper, A.E., Long, J.R., Staples, R.J., and Stavropoulos, P., *Angew. Chem.*, 2000, vol. 39, no. 13, p. 2343.
87. Morozov, I.V., Karpova, E.V., Glazunova, T.Yu., et al., *Russ. J. Coord. Chem.*, 2016, vol. 42, p. 647.
88. Hubner, K., Roesky, H.W., Noltemeyer, M., and Bohra, R., *Chem. Ber.*, 1991, vol. 124, p. 515.
89. He, X., Chen, F., Zhang, D., et al., *Z. Anorg. Allg. Chem.*, 2019, vol. 645, no. 23, p. 1341.
90. Sánchez-Féreza, F., Bayés, L., Font-Bardia, M., and Pons, J., *Inorg. Chim. Acta*, 2019, vol. 494, p. 112.
91. Iqbala, M., Sirajuddin, M., Ali, S., et al., *Inorg. Chim. Acta*, 2016, vol. 440, p. 129.
92. Iqbal, M., Ali, S., and Tahir, M.N., *J. Struct. Chem.*, 2018, vol. 59, p. 1619.
93. Ghosh, D., Dhibar, S., Dey, A., et al., *ChemSelect*, 2020, vol. 5, no. 1, p. 75.
94. Han, L.-J., Kong, Y.-J., Yan, T.-J., et al., *Dalton Trans.*, 2016, vol. 45, p. 18566.
95. Baur, A., Bustin, K.A., Aguilera, E., et al., *Org. Chem. Front.*, 2017, vol. 4, p. 5194.
96. Eremina, J.A., Lider, E.V., Sukhikh, T.S., et al., *Inorg. Chim. Acta*, 2020, vol. 510, no. 119778.
97. Mushtaq, A., Ali, S., Nawaz Tahir, M., Haider, A., et al., *Russ. J. Inorg. Chem.*, 2019, vol. 64, p. 1365.
98. Wang, K.-H. and Gao, E.-J., *Inorg. Chim. Acta*, 2018, vol. 482, p. 221.
99. Zhao, X., Liang, D., Liu, S., et al., *Inorg. Chem.*, 2008, vol. 47, no. 16, p. 7133.
100. Zhang, H.-R., Gu, J.-Z., Kirillova, M.V., and Kirillov, A.M., *Inorg. Chem. Front.*, 2021, vol. 8, p. 4209.
101. Jiang, X., Xia, H., Zhu, Y-F., et al., *Z. Anorg. Allg. Chem.*, 2011, vol. 637, nos. 14–15, p. 2273.
102. Mehrani, A., Morsali, A., and Ebrahimpour, P., *J. Coord. Chem.*, 2013, vol. 66, no. 5, p. 856.
103. Revathi, P., Mohan, J.S., Balakrishnan, T., et al., *Acta Crystallogr., Sect. E: Crystallogr. Commun.*, 2019, vol. 75, p. 134.
104. Orts-Arroyo, M., Castro, I., Lloreta, F., and Martinez-Lillo, J., *Dalton Trans.*, 2020, vol. 49, p. 9155.
105. Lazarou, K.N., Chadjistamatis, I., Terzis, A., et al., *Inorg. Chim. Acta*, 2010, vol. 363, no. 1, p. 107.
106. Le, X.-Y., Zhou, X.-H., Yu, K.-B., and Ji, L.-N., *Chin. J. Chem.*, 2000, vol. 18, p. 638.
107. Lazarou, K.N., Chadjistamatis, I., and Terzis, A., *Polyhedron*, 2010, vol. 29, no. 2, p. 833.
108. Li, D.-P., Liang, X.-Q., Xu, Y., et al., *Chin. J. Struct. Chem.*, 2013, vol. 32, p. 1724.
109. Tian, Y.-P., Zhang, X.-J., Wu, J.-Y., et al., *New J. Chem.*, 2002, vol. 26, p. 1468.
110. Ghosh, A.K., Ghoshal, D., Zangrando, E., et al., *Inorg. Chem.*, 2007, vol. 46, no. 8, p. 3057.

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