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To blessed memory of Teacher: to the 80th birthday of Prof. A.A. Pasynskii

Correlations between the Structures of Binuclear Copper(II) Tetracarboxylates with 1,4-Dioxane and the Nature of Substituent R in the Carboxylate Anion

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Abstract—The dissolution of aqueous copper(II) acetate in coordinating bidentate 1,4-dioxane (reflux) affords anhydrous mononuclear complex $Cu_2(\mu\text{-}OOCMe)_4(dioxane)_2$ (**I**) (Cu...Cu 2.5781(3) Å). The crystal of complex **I** contains contacts of the α-H atom of the CH_2 fragments of coordinated dioxane with the oxygen atom of the bridging anion with the formation of the 2D metal-organic framework (MOF). The anionic exchange reactions of the acetate bridges by pivalate or trifluoroacetate groups with the corresponding acids in boiling dioxane give 1D MOF $\{Cu_2(\mu\text{-}OOCR)_4(dioxane)\}_n$ (R = ^{t}Bu (**II**), Cu...Cu 2.5493(7) Å; CF_3 (**III**), Cu...Cu 2.6391(12) Å) characterized by the step and linear geometry, respectively. A similar reaction of $Cu_2(\mu\text{-}OOCMe)_4(OH_2)_2$ with $HOOCCF_3$ but at room temperature in the presence of crude benzene affords mononuclear complex $Cu(OOCCF_3)_2(OH_2)_3 \cdot 2$ dioxane (**IV**). Complexes **I**–**IV** are studied by elemental and X-ray diffraction analyses (CIF files CCDC nos. 2052618 (**I**), 2052619 (**II**), 2052620 (**III**), and 2052617 (**IV**)). The influence of the electronic and steric factors of substituents R on the compositions and structures of the mononuclear complexes and MOFs with 1,4-dioxane are discussed for the synthesized and known copper(II) tetracarboxylates.

Keywords: binuclear complexes, copper(II) acetate, copper(II) pivalate, copper(II) trifluoromethylacetate, bidentate O donor, metal-organic frameworks, synthesis, X-ray diffraction analysis

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INTRODUCTION

In the absence of strong donor, copper(II) carboxylates are binuclear and have the Chinese lantern structures with four bridging ligands $OOCR^-$ [1, 2]. These complexes, in particular, acetates, evoke increased interest as the starting compounds convenient for the synthesis of numerous derivatives with other bridging carboxylate anions or anions of molecules capable of deprotonating. They are characterized by unique magnetic properties (it is known that antiferromagnetism was first observed for the Cu(II) tetracarboxylate dimers with the electronic configuration d^9) and are often considered as synthetic analogs of the active part of the copper-containing proteins (with the nitrogen-containing bridging and terminal ligands) [3–5].

In addition, the copper(II) complexes containing functionalized or polydentate carboxylate anions and/or labile molecules in the axial positions of the dimer are used for the synthesis of MOFs of various dimensionality [6–11].

The most part of 3*d*-metal carboxylates contains coordination and/or solvate water molecules, which substantially affects both the substitution of water by weak donors (e.g., when constructing polymers) and occurrence of further reactions due to the high polarity and coordination ability of H_2O [12]. In this case, coordinated water is tried to substitute by polar donor molecules of the solvent (e.g, acetonitrile, THF, etc.) that can easily leave the coordination sphere of the metal during the reaction to form vacant orbitals [10]. Weakly polar bidentate 1,4-dioxane also has these properties, since it has two nucleophilic centers and is capable of direct binding to the complex forming metal as a usual terminal ligand and of forming MOF to become the μ-bridging ligand also due to intermolecular hydrogen bonds in the crystal [13–18]. The formation of a water–dioxane azeotropic mixture (T_b = 87.8°C) with allowance for the boiling point of pure dioxane (101°C) allows one to partially or completely remove H_2O from the reaction solution [19].

In this work we report the synthesis and structures of binuclear copper(II) carboxylates bearing substituents R in the carboxylate anion with various donor and steric abilities (R = Me, ^{t}Bu, and CF_3; pK_a = 4.76, 5.05, and 0.23 at 25°C in H_2O, respectively [20]). The carboxylates were synthesized by the reactions of the corresponding acids with aqueous copper acetate in boiling 1,4-dioxane followed by the removal of ~1/2 solvent volume in an argon flow.

EXPERIMENTAL

The following reagents were used: $Cu_2(OOCMe)_4(OH_2)_2$ (high-purity grade), pivalic acid (analytical grade, ACROS), and trifluoroacetic acid and 1,4-dioxane (analytical grade, Khimmed Sintez).

Synthesis of $Cu_2(\mu\text{-}OOCMe)_4(dioxane)_2$ (I). Anhydrous copper(II) acetate (1 g, 5 mmol) was dissolved in 1,4-dioxane (10 mL). The resulting blue solution was refluxed for 1 h and concentrated in an argon flow to 4 mL. The solution was kept in a refrigerator at 5°C for 2 days. The formed large single crystals were decanted from the mother liquor, washed consequently with cold benzene (10 mL) and hexane (10 mL), and dried in an argon flow. The yield of complex **I** was 1.2 g (95%) (based on the single-crystal product).

For $C_{16}H_{28}O_{12}Cu_2$

Anal. calcd., %	C, 35.62	H, 5.23
Found, %	C, 35.16	H, 5.44

IR (ν, cm^{-1}): 2961 w, 2928 w, 2900 w, 1667 w, 1608 s, 1420 s, 1367 w, 1352 m, 1293 m, 1256 m, 1204 w, 1112 s, 1074 s, 1045 m, 887 m, 863 s, 851 m, 826 m, 795 w, 725 w, 682 s, 628 s, 614 s, 521 w.

Synthesis of $\{Cu_2(\mu\text{-}OOC^tBu)_4(dioxane)\}_n$ (II). Pivalic acid (0.038 g, 0.36 mmol) was added to a solution of complex **I** (0.1 g, 0.18 mmol) in 1,4-dioxane (5 mL). The resulting blue solution was refluxed for 1 h, concentrated to 2 mL, and kept in a refrigerator at 5°C for 2 days. The formed blue single crystals were decanted from the solution, consequently washed with cold benzene (5 mL) and hexane (10 mL), and dried in an argon flow. The yield of complex **II** was 0.093 g (81%) (based on the single-crystal product).

For $C_{24}H_{44}O_{10}Cu_2$

Anal. calcd., %	C, 46.52	H, 7.16
Found, %	C, 46.13	H, 6.87

IR (ν, cm^{-1}): 2961 w, 2928 w, 2900 w, 1667 w, 1608 s, 1420 s, 1367 w, 1352 m, 1293 m, 1256 m, 1204 w, 1112 s, 1074 s, 1045 m, 887 m, 863 s, 851 m, 826 m, 795 w, 725 w, 682 s, 628 m, 614 s, 521 w.

Synthesis of $\{Cu_2(\mu\text{-}OOCCF_3)_4(dioxane)\cdot 4\ dioxane\}_n$ (III). Trifluoroacetic acid (0.042 g, 0.36 mmol) was added to a solution of complex **I** (0.1 g, 0.18 mmol) in 1,4-dioxane (5 mL). The resulting blue solution was refluxed for 1 h, concentrated to 2 mL, and kept in a refrigerator at 5°C for 2 days. The formed blue single crystals were decanted from the solution, washed consequently with cold benzene (5 mL) and hexane (10 mL), and dried in an argon flow. The yield of complex **III** was 0.13 g (86%) (based on the single-crystal product).

For $C_{20}H_{24}O_{14}F_{12}Cu_2$

Anal. calcd., %	C, 28.48	H, 2.87
Found, %	C, 28.57	H, 2.78

IR (ν, cm^{-1}): 2962 w, 2857 w, 1665 m, 1611 s, 1575 m, 1418 s, 1379 w, 1371 w, 1351 m, 1288 w, 1259 m, 1250 m, 1203 s, 1167 m, 1111 s, 1098 m, 1075 s, 1046 m, 887 m, 860 s, 795 m, 735 m, 682 s, 628 m, 612 s, 524 w.

Synthesis of $Cu(OOCCF_3)_2(OH_2)_3\cdot 2$ dioxane (IV). Trifluroacetic acid (1.14 g, 10 mmol), crude (2–3% H_2O) benzene (5 mL), and 1,4-dioxane (5 mL) were added consequently to single crystals of anhydrous copper(II) acetate (1 g, 5 mmol). The resulting blue solution was stirred at room temperature and kept in a flask with open plugs for 10 days in a draft hood. The formed blue single crystals were decanted from the solution, washed consequently with cold benzene (5 mL) and hexane (10 mL), and dried in an argon flow. The yield of complex **IV** was 1 g (38%) (based on the single-crystal product).

For $C_{12}H_{22}O_{11}F_6Cu$

Anal. calcd., %	C, 27.73	H, 4.27
Found, %	C, 27.65	H, 4.14

IR (ν, cm^{-1}): 3334 br.s, 2978 w, 2941 w, 1721 s, 1693 s, 1452 w, 1392 w, 1198 s, 1157 s, 1075 w, 870 w, 797 m, 726 m, 601 w, 418 w.

IR spectra were recorded on a Perkin-Elmer Spectrum 65 FT-IR spectrometer using the attenuated total internal reflectance (ATR) method in a frequency range of 400–4000 cm^{-1}.

X-ray diffraction (XRD) analyses of compounds **I**–**IV** were carried out using a standard procedure on a Bruker SMART Apex II automated diffractometer equipped with a CCD detector (λ_{Mo} radiation, graphite monochromator, ω scan mode). Structure refinement was performed using the SHELXTL PLUS program package (PC version) [21–24]. The structures were determined by a direct method and refined by least squares in the anisotropic approximation for

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

Parameter	Value			
	I	**II**	**III**	**IV**
Empirical formula	$C_{16}H_{28}O_{12}Cu_2$	$C_{24}H_{44}O_{10}Cu_2$	$C_{20}H_{24}O_{14}F_{12}Cu_2$	$C_{12}H_{22}O_{11}F_6Cu$
FW	539.46	619.67	843.47	519.84
Color	Blue	Blue	Blue	Blue
T, K	100(2)	100(2)	100(2)	150(2)
Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	*Pnnm*	$P\bar{1}$
a, Å	8.0498(2)	8.9250(6)	10.2916(3)	5.9408(14)
b, Å	8.0139(2)	9.3713(6)	14.7224(3)	12.026(3)
c, Å	16.6094(3)	10.4172(8)	9.6652(3)	14.671(3)
α, deg	90	85.567(3)	90	101.472(10)
β, deg	101.3044(7)	68.022(3)	90	99.262(9)
γ, deg	90	70.991(3)	90	98.876(10)
V, Å^3	1050.69(4)	762.92(9)	1464.44(7)	994.8(4)
Z	2	1	2	2
ρ_{calc}, mg/m^3	1.705	1.349	1.913	1.735
μ, mm^{-1}	2.085	1.440	1.595	1.206
F(000)	354	326	844	530
Crystal size, mm	0.26 × 0.24 × 0.22	0.24 × 0.22 × 0.20	0.22 × 0.20 × 0.18	0.24 × 0.22 × 0.20
Scan θ range, deg	3.57–30.52	2.60–28.00	2.41–30.00	1.76–27.00
Ranges of reflection indices	$-11 \le h \le 11$, $-11 \le k \le 11$, $-23 \le l \le 20$	$-11 \le h \le 11$, $-12 \le k \le 12$, $-13 \le l \le 12$	$-14 \le h \le 12$, $-20 \le k \le 19$, $-13 \le l \le 13$	$-7 \le h \le 7$, $-15 \le k \le 15$, $-18 \le l \le 18$
Number of reflections	13402	7406	18092	7665
Number of independent reflections (R_{int})	3211 (0.0245)	3473 (0.0339)	2249 (0.0507)	4271 (0.0781)
GOOF	1.005	1.142	1.068	0.982
R ($I > 2\sigma(I)$)	$R_1 = 0.0229$, $wR_2 = 0.0586$	$R_1 = 0.0429$, $wR_2 = 0.1123$	$R_1 = 0.0731$, $wR_2 = 0.1689$	$R_1 = 0.0798$, $wR_2 = 0.1584$
R (for all reflections)	$R_1 = 0.0268$, $wR_2 = 0.0601$	$R_1 = 0.0502$, $wR_2 = 0.1156$	$R_1 = 0.0960$, $wR_2 = 0.1837$	$R_1 = 0.1500$, $wR_2 = 0.1867$
Residual electron density (max/min), e Å^3	0.568/–0.372	0.824/–0.926	0.914/–1.232	0.810/–0.913

non-hydrogen atoms. The positions of the hydrogen atoms in complexes **I** and **IV** were revealed from the difference Fourier series and refined isotropically, whereas those for complexes **II** and **III** were determined geometrically by the riding model. The crystallographic data and structure refinement for compounds **I**–**IV** are presented in Table 1. Selected bond lengths and bond angles are given in Table 2.

The structural data for the complexes were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2052618 (**I**), 2052619 (**II**),

Table 2. Selected bond lengths (Å) and bond angles (deg) in complexes **I–IV***

Bond	*d*, Å	Bond	*d*, Å
I			
Cu(1)–O(2)	1.9578(10)	Cu(1)–O(3)	1.9605(9)
Cu(1)–O(1)	1.9607(9)	Cu(1)–O(4)	1.9628(10)
Cu(1)–O(5)	2.2263(9)	Cu(1)–Cu(1)$^{\#1}$	2.5781(3)
II			
Cu(1)–O(3)	1.955(3)	Cu(1)–O(1)	1.953(2)
Cu(1)–O(4)	1.962(3)	Cu(1)–O(2)	1.962(2)
Cu(1)–O(5)	2.188(2)	Cu(1)–Cu(1)$^{\#1}$	2.5493(7)
III			
Cu(1)–O(2)#1	1.966(3)	Cu(1)–O(2)	1.966(3)
Cu(1)–O(1)	1.967(3)	Cu(1)–O(1)$^{\#1}$	1.967(3)
Cu(1)–O(3)	2.117(4)	Cu(1)–Cu(1)$^{\#2}$	2.6391(12)
IV			
Cu(1)–O(1)	1.930(5)	Cu(1)–O(3)	1.935(5)
Cu(1)–O(6)	1.940(5)	Cu(1)–O(5)	1.950(5)
Cu(1)–O(11)	2.190(5)		
Angle	ω, deg	Angle	ω, deg
I			
O(2)Cu(1)O(3)	89.80(4)	O(2)Cu(1)O(1)	170.19(4)
O(3)Cu(1)O(1)	89.89(4)	O(2)Cu(1)O(4)	89.21(4)
O(3)Cu(1)O(4)	170.13(4)	O(1)Cu(1)O(4)	89.41(4)
O(2)Cu(1)O(5)	97.11(4)	O(3)Cu(1)O(5)	92.66(4)
O(1)Cu(1)O(5)	92.71(4)	O(4)Cu(1)O(5)	97.21(4)
O(2)Cu(1)Cu(1)$^{\#1}$	88.19(3)	O(3)Cu(1)Cu(1)$^{\#1}$	82.83(3)
O(1)Cu(1)Cu(1)$^{\#1}$	82.04(3)	O(4)Cu(1)Cu(1)$^{\#1}$	87.32(3)
O(5)Cu(1)Cu(1)$^{\#1}$	173.05(3)	C(1)O(1)Cu(1)	125.59(9)
II			
O(3)Cu(1)O(1)	90.97(12)	O(3)Cu(1)O(4)	170.86(9)
O(1)Cu(1)O(4)	89.10(11)	O(3)Cu(1)O(2)	88.96(11)
O(1)Cu(1)O(2)	170.75(9)	O(4)Cu(1)O(2)	89.50(11)
O(3)Cu(1)O(5)	93.61(9)	O(1)Cu(1)O(5)	93.96(9)
O(4)Cu(1)O(5)	95.50(9)	O(2)Cu(1)O(5)	95.28(9)
O(3)Cu(1)Cu(1)$^{\#1}$	84.94(7)	O(1)Cu(1)Cu(1)$^{\#1}$	85.05(7)
O(4)Cu(1)Cu(1)$^{\#1}$	85.96(7)	O(2)Cu(1)Cu(1)$^{\#1}$	85.73(7)
O(5)Cu(1)Cu(1)$^{\#1}$	178.23(7)	C(1)O(1)Cu(1)	122.7(2)
III			
O(2)$^{\#1}$Cu(1)O(2)	168.99(16)	O(2)$^{\#1}$Cu(1)O(1)	89.02(14)
O(2)Cu(1)O(1)	89.92(14)	O(2)$^{\#1}$Cu(1)O(1)$^{\#1}$	89.92(14)
O(2)Cu(1)O(1)$^{\#1}$	89.02(14)	O(1)Cu(1)O(1)$^{\#1}$	168.91(16)
O(2)$^{\#1}$Cu(1)O(3)	95.51(8)	O(2)Cu(1)O(3)	95.51(8)
O(1)Cu(1)O(3)	95.54(8)	O(1)$^{\#1}$Cu(1)O(3)	95.54(8)
O(2)$^{\#1}$Cu(1)Cu(1)$^{\#2}$	84.49(8)	O(2)Cu(1)Cu(1)$^{\#2}$	84.49(8)
O(1)Cu(1)Cu(1)$^{\#2}$	84.46(8)	O(1)$^{\#1}$Cu(1)Cu(1)$^{\#2}$	84.46(8)
O(3)Cu(1)Cu(1)$^{\#2}$	180.000(1)	C(1)O(1)Cu(1)	121.1(3)
IV			
O(1)Cu(1)O(3)	178.0(2)	O(1)Cu(1)O(6)	89.9(2)
O(3)Cu(1)O(6)	90.3(2)	O(1)Cu(1)O(5)	88.8(2)
O(3)Cu(1)O(5)	90.6(2)	O(6)Cu(1)O(5)	166.75(19)
O(1)Cu(1)O(11)	90.51(19)	O(3) Cu(1)O(11)	91.43(19)
O(6)Cu(1)O(11)	96.4(2)	O(5)Cu(1)O(11)	96.8(2)
C(1)O(1)Cu(1)	120.2(5)	C(3)O(3)Cu(1)	121.2(5)
O(1)Cu(1)O(3)	178.0(2)	O(1)Cu(1)O(6)	89.9(2)
O(3)Cu(1)O(6)	90.3(2)	O(1)Cu(1)O(5)	88.8(2)

* Symmetry transforms used for the generation of equivalent atoms: $^{\#1}$ $-x + 1, -y + 1, -z + 1$ (**I**); $^{\#1}$ $-x + 3, -y + 1, -z + 1$ (**II**); $^{\#1}$ $-x + 1, -y + 1, z$; $^{\#2}$ $-x + 1, -y + 1, -z + 1$ (**III**).

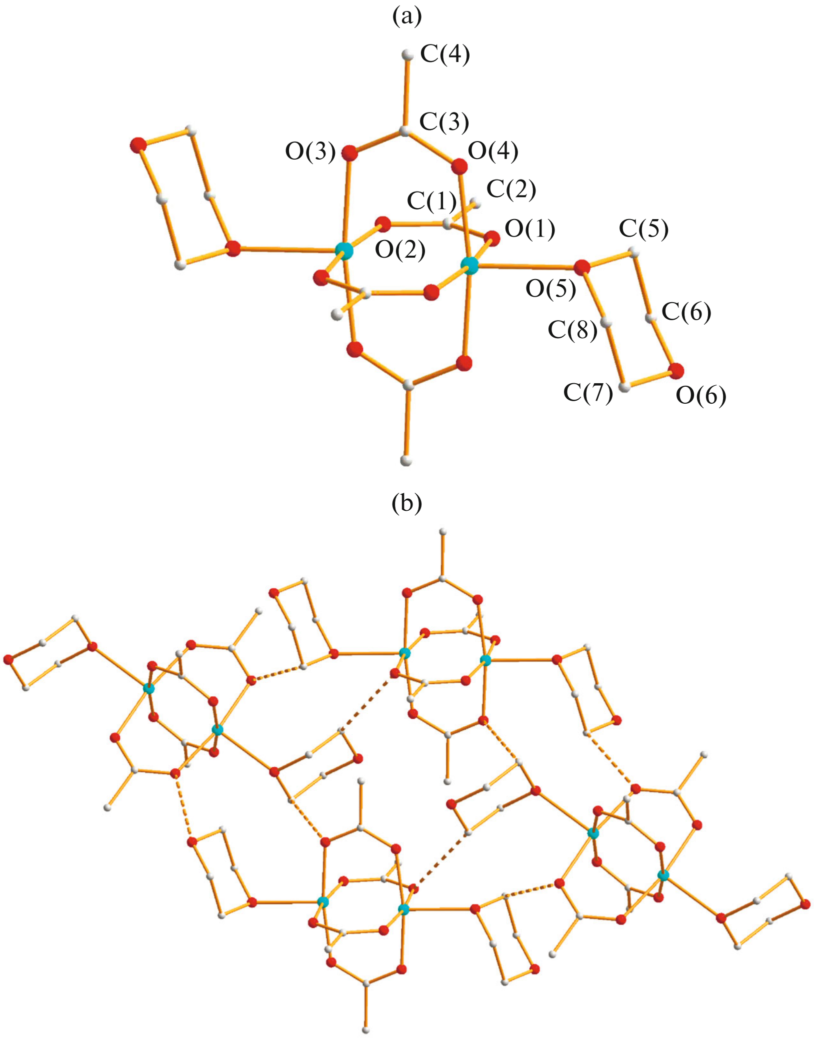

Fig. 1. (a) Structure of dimer **I** and (b) the fragment of its molecular packing in the crystal. Colors of atoms: copper is blue, oxygen is red, and carbon is gray.

2052620 (**III**), and 2052617 (**IV**); http://www.ccdc.cam.ac.uk/).

RESULTS AND DISCUSSION

The dissolution of binuclear anhydrous copper(II) acetate in 1,4-dioxane followed by reflux for 1 h and removal of 50% solvent was found to result in the formation of the dimer $Cu_2(\mu\text{-}OOCMe)_4(dioxane)_2$ (**I**). According to the XRD data, in centrosymmetric complex **I** two Cu(II) atoms are arranged at a short nonbonding distance of 2.5781(3) Å and are joined by four acetate bridges (Cu(1)–O(1) 1.9607(9), Cu(1)–O(2) 1.9578(10), Cu(1)–O(3) 1.9605(9), and Cu(1)–O(4) 1.9628(10)), and the axial positions in the dimer are occupied by the oxygen atoms of axially coordinated dioxane (Cu(1)–O(5) 2.2263(9) Å) (Table 2, Fig. 1a).

The crystal packing of the molecules of complex **I** contains fairly weak contacts of the α-H atoms of the CH_2 fragments of coordinated dioxane with the oxygen atom of the bridging acetate anion (C(7)...O(4) 3.366 Å) forming the single crystal (Fig. 1b). Note that the procedure proposed for the synthesis of complex **I** results in the removal of coordinated water molecules that are present in the initial copper acetate.

The reaction of anhydrous complex **I** dissolved in dioxane with pivalic acid on reflux affords blue single crystals of complex **II**, which is centrosymmetric as complex **I** according to the XRD data (at 100 K). However, unlike complex **I**, complex **II** is a polymer with the bridging dioxane molecule (Cu–O(5) 2.188(2), Cu...Cu 2.5493(7), and Cu–μ-O_{OOC^tBu} 1.953(2)–1.962(2) Å) (Table 2, Fig. 2).

The copper atoms are packed in parallel to form the stepped 1D polymer in which the distances of the nearby lying metal atoms of the adjacent dimers are

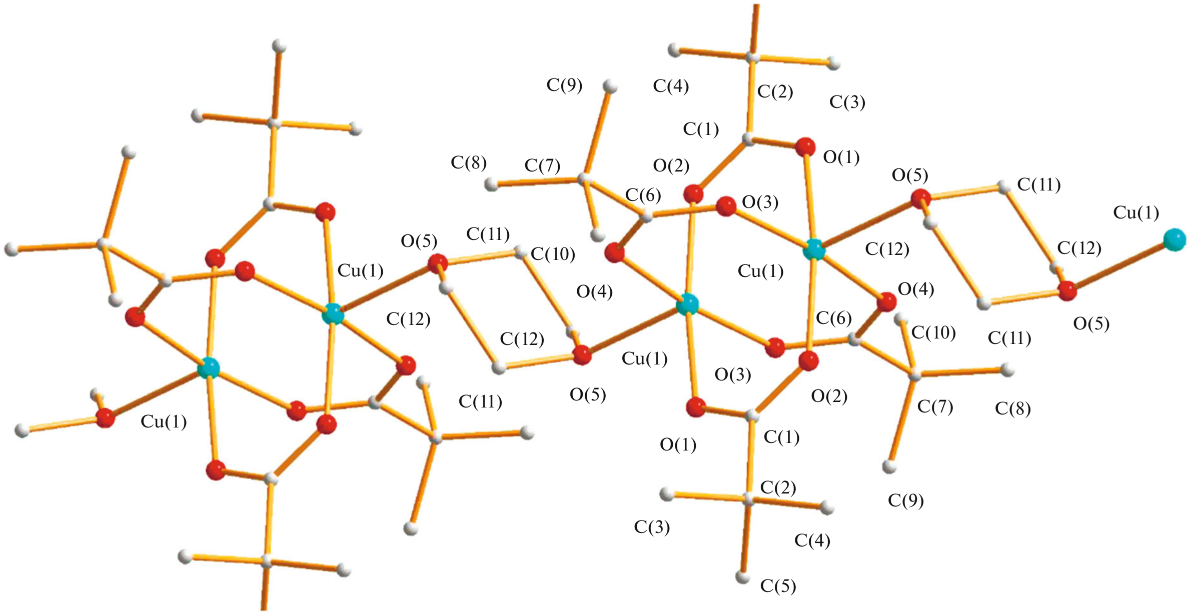

Fig. 2. Fragment of polymer **II**.

6.473 Å, and the angle between the lines of Cu_2 and two O(5) atoms of dioxane is 51.4° (Fig. 3).

A similar exchange reaction of bridged acetates by the anions of stronger trifluoroacetic acid gives blue single crystals of polymer **III**. According to the XRD data, compound **III** (Table 2, Fig. 3a) is a polymer in which the centrosymmetric dimers Cu_2 (Cu...Cu 2.6391(12), Cu–μ-O_{OOCCF3} 1.966(3)–1.967(3) Å) are connected by the bidentate dioxane molecule (Cu–O(3) 2.117(4) Å). Unlike complex **II**, in polymer **III** the copper and oxygen atoms of the dioxane molecules lie on one line and the coordinated dioxane molecules are planar and form an angle with the $Cu_2O(1)$ plane (40.8°). This change in the geometry compared to polymer **II** along with a similar steric size of substituent R in the carboxylate anion is related to a significant decrease in the donor ability of the anions of strong trifluoroacetic acid (as compared to fairly weak pivalic acid [20]), which results in a noticeable change in the M...M distances and participation of an additional electron pair in the M–$O_{dioxane}$ binding.

Note that the closest contacts of the solvate dioxane molecules in the crystalline cell are F(4)...O(4) (3.042 Å).

Single crystals of mononuclear blue complex **IV** were obtained by the reaction of trifluoroacetic acid with single crystals of anhydrous copper acetate followed by the addition of crude benzene and dioxane at room temperature.

According to the XRD data for complex **IV** (Table 2, Fig. 4a), the metal atom has the trigonal bipyramidal environment typical of copper(II) and similar to that observed in the binuclear compounds. Two oxygen atoms belonging to two *syn–syn*-coordinated anions (Cu–O 1.930(5), 1.935(5) Å) are localized in the axial positions of complex **IV**. The equatorial positions are occupied by three oxygen atoms of the water molecules, one of which forms hydrogen bonds with the oxygen atoms of the anions of the nearby lying molecule of the complex (Cu–O(7) 2.190(5), O...O 2.72, 2.74 Å), whereas two other water molecules are bound to the oxygen atoms of the solvate dioxane molecules (Cu–O 1.940(5), 1.950(5), O...O 2.65–2.81 Å). As a result, a 3D polymer is formed due to the network of intermolecular hydrogen bonds, where the metal atoms are arranged on one line at a distance of 5.941 Å (Fig. 4b).

It is noteworthy that similar reactions of anhydrous nickel(II) and cobalt(II) acetates with $HOOCCF_3$ in the presence of benzene and/or using crystallization at room temperature give single crystals of complexes $\{M(OOCCF_3)_2(OH_2)_4 \cdot [O(CH_2CH_2)_4O]_2\}_n$ (M = Ni, Co) [25, 26].

According to the CCDC data, there is a restricted number of compounds of copper(II) carboxylates with coordinated dioxane molecules, the geometry of which is determined by the steric and electronic nature of substituent R in the carboxylate anion and specific features of binding of the solvate solvent molecules in the crystal [27]. In spite of different temperatures at which XRD was carried out, it is evident that the introduction of the donor substituents R (R = Me, Et, ^{t}Bu, and $CH_2{}^t$Bu) compared to the acceptor substituents (R = Ph(3-I), CH_2O–$Ph(2,4-Cl_2)$, C_6F_5, and CF_3) results in an appreciable elongation of the metal–metal distances accompanied by the shortening of the

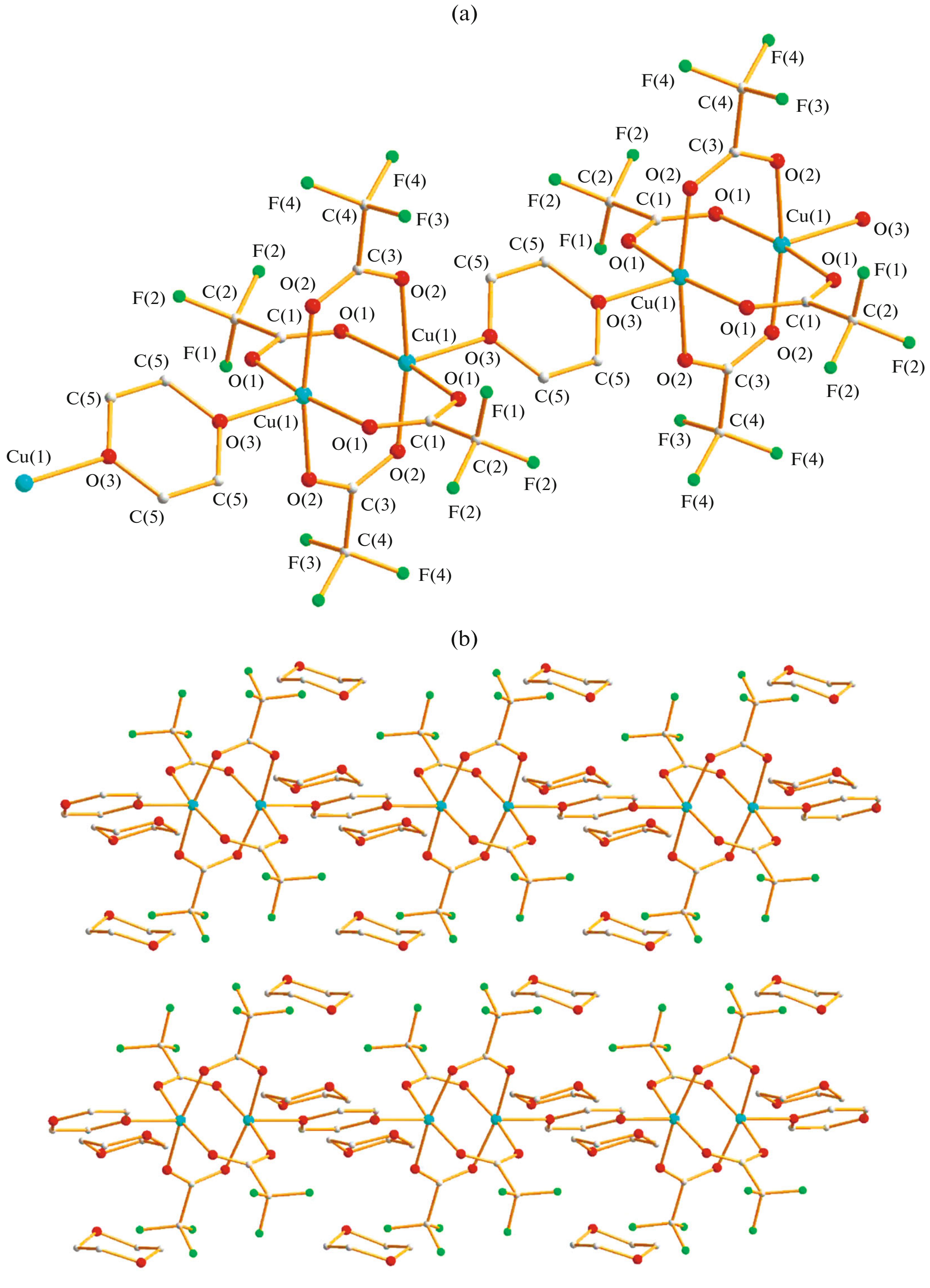

Fig. 3. (a) Structure of polymer **III** and (b) the fragment of its molecular packing in the crystal. Colors of atoms: copper is blue, fluorine is green, oxygen is red, and carbon is gray.

$M-O_{axial}$ bonds of coordinated dioxane with almost equal bonds lengths of the metal with oxygen of the carboxylate anions (Table 3).

Thus, it is found that binuclear copper(II) carboxylates refluxed in dioxane lose the coordinated water molecule and their geometries correlate with specific

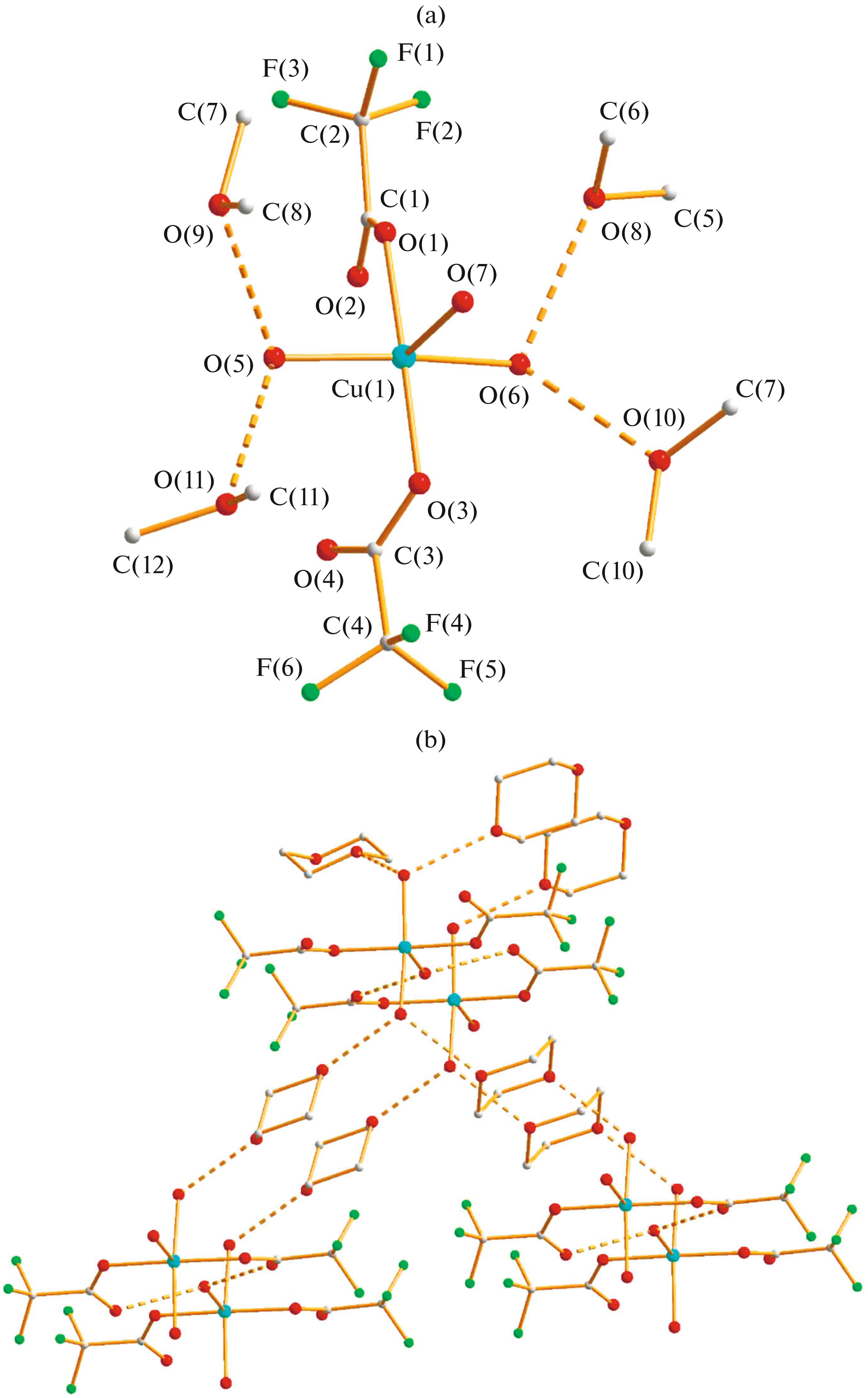

Fig. 4. (a) Independent part of complex **IV** and (b) the fragment of its molecular packing in the crystal. Colors of atoms: copper is blue, fluorine is green, oxygen is red, and carbon is gray.

features of the electronic and steric properties of substituent R in the bridging carboxylate anion.

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Table 3. Geometry of binuclear copper(II) tetracarboxylates with 1,4-dioxane

Compound, structure (T_{XRD}, K)	M...M, Å	M–O_{axial}, Å	M–μ-O_{OOCR}, Å	References
$Cu_2(\mu\text{-}OOCMe)_4(dioxane)_2$, monomer (100)	2.5781	2.226	1.958–1.963	This work
$Cu_2\{\mu\text{-}OOC[Ph\text{-}(3\text{-}I)]\}_4(dioxane)_2 \cdot 3$ dioxane, monomer (100)	2.609	2.206	1.950–1.972	28
$Cu_2\{\mu\text{-}OOC[CH_2O\text{-}Ph(2,4\text{-}Cl_2)]\}_4(dioxane)_2 \cdot 2$ dioxane, monomer (295)	2.617	2.195	1.960–1.968	29
$\{Cu_2(\mu\text{-}OOC^tBu)_4(dioxane)\}_n$, polymer (295)	2.560	2.204	1.946-1.959	30
$\{Cu_2(\mu\text{-}OOC^tBu)_4(dioxane)\}_n$, polymer (100)	2.5492	2.188	1.955–1.962	This work
$\{Cu_2[\mu\text{-}OOC(CH_2{}^tBu)]_4$ (dioxane)$\}_n$, polymer (295)	2.553	2.198	1.953–1.964	30
$\{Cu_2(\mu\text{-}OOCCEt)_4(dioxane)\}_n$, polymer (295)	2.563	2.227	1.950–1.958	31
$\{Cu_2(\mu\text{-}OOCC_6F_5)_4(dioxane) \cdot 2dioxane\}_n$, polymer (295)	2.616	2.137	1.948–1.963	32
$\{Cu_2(\mu\text{-}OOCCF_3)_4(dioxane) \cdot 4dioxane\}_n$, polymer (100)	2.6391	2.117	1.966–1.967	This work

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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