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Synthesis, crystal structure and thermal stability of new copper(II) trichloroacetate complexes

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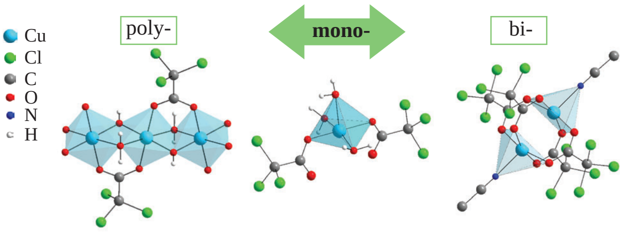
We have synthesized two novel complexes of copper(II) trichloroacetate, $Cu_2(CCl_3COO)_3(OH)(H_2O)_4{\cdot}H_2O$ and $Cu(CCl_3COO)_2(MeCN)$, and determined their crystal structures and thermal stability. While the complex with acetonitrile has a discrete binuclear paddle-wheel structure, typical of copper carboxylates, the aqua-hydroxo complex belongs to a novel unique chain–molecular type of basic copper complexes.

Topological diversity of copper trichloroacetate complexes



Keywords: basic copper salts, trichloroacetate, paddle wheel, acetonitrile solvate, crystal structure, thermal analysis.

Ligands with carboxylate groups are commonly used for two main reasons. First, they strongly bind to metal centers due to electrostatic interactions. Second, they introduce certain coordination flexibility that allows them to adopt different coordination modes that fit most metal environments and crystal packing requirements.[1–3] Carboxylate ligands allow the crystal system to fine-tune the topology and, ultimately, properties. In particular, for the widely studied acetate ligand, it has been proved that partial hydrolysis of copper is a successful tactic for increasing the topological diversity of copper acetate complexes.[4–6] An increase in the dimensionality of the crystal structure could lead to the formation of an extended magnetic system. Therefore, this possibility of controlling the magnetic exchange interactions between copper ions through bridging ligands has attracted the attention of researchers.

Most of the explored copper carboxylates have a paddle wheel-type structure (‘Chinese lantern’).[7] However, there are far fewer examples of compounds with chain topology, and as far as we know, only a few compounds with this topology have been studied structurally.[4–6,8–12] In the cited studies,[13–16] the various properties of copper(II) trichloroacetate trihydrate were investigated, and the crystals of this substance were described as ‘blue hexagonal flat plates.’

In this communication, we report the synthesis and crystal structure of two new complexes based on copper(II) trichloroacetate with crystallographic formulae $Cu_2(CCl_3COO)_3(OH)(H_2O)_4{\cdot}H_2O$ **1** and $Cu(CCl_3COO)_2(MeCN)$ **2**.

A polycrystalline sample of complex **1** was prepared by the reaction of a slight excess of $(CuOH)_2CO_3$ with aqueous CCl_3COOH.[†] This method allows one to obtain high-quality single crystals. The following processes proceed in the solution:

$$(CuOH)_2CO_3 + 2H^+ \rightleftarrows 2CuOH^+ + H_2O + CO_2, \qquad (1)$$

$$CuOH^+ + H^+ \rightleftarrows Cu^{2+} + H_2O. \qquad (2)$$

Under conditions of acid deficiency, equilibrium (2) shifts towards the reverse reaction, that is, hydrolysis of the copper cation, and the $CuOH^+$ form prevails in the solution, which leads to the formation of a chain structure. An increase in temperature promotes this process. Therefore, the synthesis can be carried out with slight heating up to 60 °C.

As a result of these processes, compound **1** was formed.[†] Compound **1** is more stable in air than copper(II) trichloroacetate trihydrate. The solubility of complex **1** in diethyl ether, acetone and ethanol is relatively high. Upon dissolution in water, subsequent hydrolysis occurs with the formation of an insoluble white precipitate. Substance **1** is less soluble in dioxane, so it can be used to wash crystals from the mother liquor.

Compound **2** was obtained by recrystallization of $Cu(CCl_3COO)_2(H_2O)_3$ in acetonitrile.[‡]

It was established by X-ray crystallography[§] that complex **1** consists of electrically neutral monomers and infinite chains.

[†] *$Cu_2(CCl_3COO)_3(OH)(H_2O)_4{\cdot}H_2O$* **1**. $(CuOH)_2CO_3$ (2 mmol) was added to a concentrated aqueous solution (5 ml) of trichloroacetic acid, CCl_3COOH, (5.5 mmol) with continuous stirring at room temperature. The suspension was then filtered, and the clear solution was stored in a desiccator for several days, after which pale blue needle crystals precipitated. FT-IR (ATR) (ν/cm^{-1}): 3624 and 3581 (OH), 1635, 1605, 1400 and 1354 (COO), 962 (C–C), 875, 837, 750 and 685 (CCl_3). Found (%): C, 10.07; H, 1.45; Cl, 42.01. Calc. for $C_6H_{11}Cl_9Cu_2O_{12}$ (%): C, 9.98; H, 1.53; Cl, 44.28.

[‡] *$Cu(CCl_3COO)_2(MeCN)$* **2**. Copper(II) trichloroacetate trihydrate, $Cu(CCl_3COO)_2(H_2O)_3$, was synthesized according to the published procedure.[13–16] Recrystallization of $Cu(CCl_3COO)_2(H_2O)_3$ (1 mmol) in acetonitrile (1.57 g, 2.00 ml) afforded compound **2** as hygroscopic green crystals. FT-IR (ATR) (ν/cm^{-1}): 2995 and 2933 (Me), 2305 (C≡N), 2278 (CCN), 1682 and 1365 (COO), 1438 and 1030 (Me), 970 and 930 (C–C), 849, 829, 750 and 687 (CCl_3). Found (%): C, 16.80; H, 0.86; N, 3.39; Cl, 49.05. Calc. for $C_6H_3Cl_6CuNO_4$ (%): C, 16.78; H, 0.70; N, 3.26; Cl, 49.54.

[§] *Crystal data for* **1**. $C_6H_{11}Cl_9Cu_2O_{12}$, $M = 721.28$, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.9507(4)$, $b = 6.10380(10)$ and $c = 28.8258(9)$ Å, $\beta = 95.014(3)°$, $V = 2269.92(11)$ Å^3, $T = 295(2)$ K, $Z = 4$, $\mu = 12.563$ mm^{-1}. 15000 reflections were measured, and 3984 unique reflections ($R_{int} = 0.0621$) were used in all calculations. The final R factor was 0.0504 [$I > 2\sigma(I)$]. Crystal with dimensions 0.23 × 0.11 × 0.09 mm was selected.

Crystal data for **2**. $C_6H_3Cl_6CuNO_4$, $M = 429.33$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.8536(8)$, $b = 9.2125(8)$ and $c = 9.4782(10)$ Å, $\alpha = 72.301(7)°$, $\beta = 86.568(8)°$, $\gamma = 70.718(7)°$, $V = 694.47(12)$ Å^3, $T = 293(2)$ K, $Z = 1$, $\mu = 2.727$ mm^{-1}. 9646 reflections were measured, and

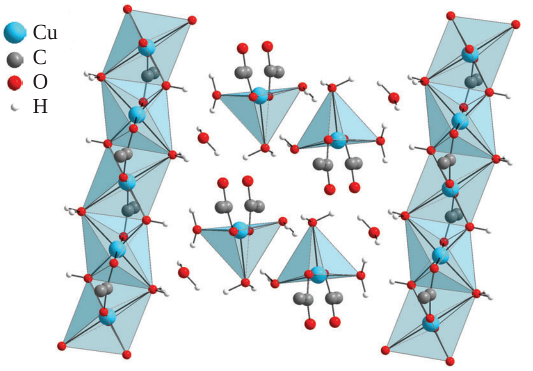


Figure 1 Mutual arrangement of the chain and discrete fragments in the crystal structure of complex **1**. Chlorine atoms are omitted for clarity.

The mutual arrangement of fragments in the structure is shown in Figure 1. The monomeric fragment is structurally identical to copper(II) trichloroacetate trihydrate,[16] in which the copper polyhedron is a square pyramid with a base of oxygen atoms of two trichloroacetate ligands and two water molecules. The third water molecule occupies an apical position.

The chain fragment is formed by six-coordinated copper cations linked through the CCl_3COO^- and OH^- anions and H_2O molecules (Figure 2). The copper coordination polyhedron is a distorted octahedron. Four oxygen atoms from two hydroxide ions and two carboxylate ions are coordinated with the copper ion in the basal plane, and oxygen atoms of two water molecules occupy two apical positions, resulting in three different pairs of Cu–O distances. Thus, the copper ion exhibits the (2 + 2 + 2) coordination type, consistent with the Jahn–Teller distortion; other examples of this coordination have been observed and reported.[17]

A comparison of the bond lengths in the resulting compound **1** with the published data is shown in Table S1 (see Online Supplementary Materials). The bond distances between the copper atom and the oxygen atom of the hydroxide ion [1.925(3)–1.931(3) Å] are slightly shorter than the length of the Cu–O bond between the copper(II) ion and the oxygen atom of a bridging carboxylate ligand [2.008(4)–2.025(4) Å], which is typical of bidentate-coordinated trichloroacetate ligands. It is noteworthy that the Cu–O distances to the oxygen atom of water in the chain [2.364(4)–2.428(4) Å] are significantly longer than the corresponding distance to the negatively charged OH^- ion. A slight distortion is present not only in the bond lengths but also in the angles between them. The angles between the axes of the octahedron are not right. They range from 83.66(14) to 96.54(14)°, so the polyhedra are connected with a slope: the torsion angles between faces with a common edge are 51.09(13) and 100.61(16)°, and the Cu···Cu···Cu angle is 178.77(5)°. The Cu···Cu distance is 3.05207(5) Å inside the chains of the edge-sharing CuO_6 octahedra. Similar chains of Cu atoms have also been described in the literature,[8,9] with the same distance between copper centers [3.0433(3)–3.0792(4) Å].

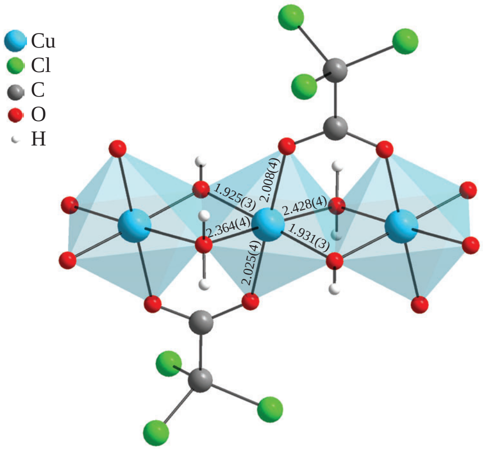


Figure 2 The polymeric fragment of the crystal structure of complex **1**. The Cu–O bond lengths in copper polyhedra are given in Å.

Since magnetic exchange can occur through the orbitals of intermediate atoms, the most important is the value of the Cu–O–Cu angle at the bridging hydroxide ligand. This value was found to be 104.65(17)° in complex **1**, which is below the critical angle (about 110°) according to the Goodenough–Kanamori–Anderson (GKA) rules. Therefore, it is assumed that the exchange will be ferromagnetic.

In the monomer, such a Cu–O bond length is observed only with the water O(9) atom [2.350(4) Å] at the apex of the square pyramid. The other Cu–O distances are approximately equal, despite the fact that the base of the square pyramid is formed by oxygen atoms of both water molecules [1.953(4)–1.997(4) Å] and carboxylate groups [1.922(4)–1.949(4) Å].

Complex **1** is unique because it combines two structural motives, molecular and chain. Monomers and chains are stacked into layers along the *a*-axis. In the space between the fragments, there are uncoordinated water molecules. Packing takes place through a network of hydrogen bonds. The fragments are linked to each other by weak hydrogen bonds: the O···O distances range from 2.737(6) to 3.014(6) Å, and the O···Cl distances range from 3.447(5) to 3.650(5) Å.

According to the X-ray diffraction data, complex **2** is structurally similar to many known copper haloacetates.[7] The bond lengths in the obtained compound **2** are compared with the published values in Table S2. Four bridging carboxylate ligands connect two Cu atoms: the complex consists of binuclear molecules (Figure 3)

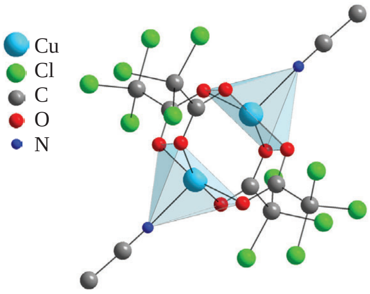


Figure 3 The molecular fragment of the crystal structure of complex **2**.

3300 unique reflections ($R_{int} = 0.0507$) were used in all calculations. The final R factor was 0.0418 [$I > 2\sigma(I)$]. Crystal with dimensions 0.09 × 0.095 × 0.1 mm was selected.

A single crystal of compound **2** was coated with epoxy for analysis. A single crystal of compound **1** was analyzed without special conditions. Data for compounds **1** and **2** were collected using an STOE diffractometer, a Pilatus100K detector, focusing mirror collimation of CuKα radiation ($\lambda = 1.54186$ Å) for compound **1** and MoKα radiation ($\lambda = 0.71073$ Å) for compound **2** and the rotation method mode. STOE X-AREA software was used for cell refinement and data reduction. Data collection and image processing were performed using an X-Area 1.67 (STOE & Cie GmbH, Darmstadt, Germany, 2013). Intensity data were scaled using LANA (part of the X-Area) to minimize differences in the intensities of symmetry-equivalent reflections (multi-scan method).

The structures were solved and refined with the SHELX[23] program. Non-hydrogen atoms were refined using the anisotropic full-matrix least-square procedure. Hydrogen atoms were placed in calculated positions and allowed to ride on their parent atoms. Molecular geometry calculations were performed with the SHELX program, and molecular plots were prepared using the DIAMOND[24] software.

CCDC 1982631 and 2093199 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

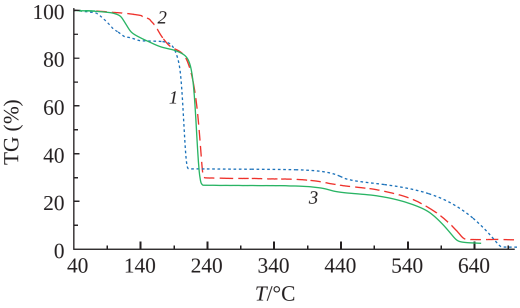


Figure 4 TG curves for (*1*) complex **1**, (*2*) complex **2** and (*3*) copper(II) trichloroacetate trihydrate.

with Cu–O distances from 1.964(3) to 1.973(3) Å, which is in the expected range for this class of compounds.[18–21] In addition, the acetonitrile nitrogen atom occupies the apical position with a Cu–N distance of 2.158(4) Å, leading to the formation of a slightly distorted square-pyramidal polyhedron. Four carboxylate oxygen atoms form the base of the pyramid. The copper atom in complex **2** is displaced by 0.2622 Å from the basal plane towards the apical ligand with apical O–Cu–N angles from 96.2(1) to 96.7(1)°, cisoid O–Cu–O angles from 88.5(1) to 90.3(1)° and transoid O–Cu–O angles in the range of 168.2(1)–168.5(1)°. The N–Cu···Cu fragment is linear with an angle of 175.5(1)°. The total span of the Cu–O–C–O–Cu bridge remains almost constant (6.411 Å). The Cu···Cu distance is 2.7514(12) Å and is typical for CuO_4N units. All bond lengths and angles agree well with the values in related complexes.[22] The 'lanterns' are linked through van der Waals interactions. The binuclear fragments form layers parallel to the *ab* plane, and the CCl_3 groups are directed to the interplanar space.

TG experiments indicated that the decomposition patterns for complexes **1**, **2** and copper(II) trichloroacetate trihydrate are very similar. From the thermograms shown in Figure 4, three main processes can be observed: solvent removal, destruction of the carboxylate group and reduction of copper to the monovalent state. Mass spectra of the gaseous products of decomposition reaction were recorded for several mass numbers (*m*/*z*) (Table S3 and Figure S1).

Dehydration of complex **1** starts at about 55 °C. Desolvation of complex **2** occurs at temperatures from about 120 °C. The second observable weight loss step is ascribed to the destruction of the carboxylate group to form a mixture of copper(I) and copper(II) chlorides. The corresponding decomposition temperature of the complex **1** (about 170 °C) is 20 °C lower than that of the trihydrate and complex **2** (about 190 °C). All curves demonstrate a synchronous weight loss at a temperature of about 450 °C, which corresponds to the formation of CuCl. Upon further heating, the solid residues sublimate until the samples completely evaporate.

IR studies of complexes **1** and **2** (Figure S2) allowed us to conclude that the vibrations of the C–C and C–Cl bonds are insensitive to changes in the coordination sphere. They coincide with the corresponding vibrations in $Cu(CCl_3COO)_2(H_2O)_3$ (Table S4).

The shape and position of absorption bands related to symmetric [ν_s(COO)] and asymmetric [ν_{as}(COO)] stretching vibrations of bonds in the carboxyl group correlate with the geometry of the complexes. Carboxylate ions perform different functions in different compounds. Two CCl_3COO^- ligands are monodentate and terminal in $Cu(CCl_3COO)_2(H_2O)_3$. Four bidentate trichloroacetate groups act as bridges in complex **2**. Compound **1** combines both types of coordination: one bidentate ligand is in the chain fragment, and two monodentate ligands are in the molecular fragment. The absorption bands ν_s(COO) and ν_{as}(COO) in the spectrum of complex **2** are shifted to shorter wavelengths relative to the bands in the spectra of compound **1** and $Cu(CCl_3COO)_2(H_2O)_3$. The peak profiles in the spectra of these compounds set the peak profile in the spectrum of complex **1**.

In the IR spectra, the differences between the compounds are noticeable in the region of 2700–3650 cm^{-1}, corresponding to the ν(OH) vibrations. The absence of absorption in this region indicates the absence of water molecules in the sample of complex **2**. The narrow absorption bands in the spectrum of complex **1** correspond to stretching vibrations of OH^- groups that are not involved in the formation of hydrogen bonds. Therefore, we can conclude that bridging hydroxyl groups do not form hydrogen bonds.

Thus, it can be argued about the influence of the synthesis conditions on the composition of the products. A change in the ratio of reagents (acid deficiency) leads to the formation of new structural fragments due to hydrolysis. Therefore, the new compound, $Cu_2(CCl_3COO)_3(OH)(H_2O)_4 \cdot H_2O$ **1**, with a unique crystal structure is formed. Copper carboxylates of the chain type are quite rare and relatively new, and there are no data in the literature on the structure of copper(II) complexes that combine chain and mononuclear fragments.

According to the GKA rules, we predicted the appearance of ferromagnetic exchange in the chain fragment of complex **1**. This property is the second uniqueness of the compound since such chains are usually antiferromagnetic. The magnetic behavior of compound **1** with a mixed-type structure requires further research.

Recrystallization of $Cu(CCl_3COO)_2(H_2O)_3$ from acetonitrile leads to the formation of a new compound $Cu(CCl_3COO)_2(MeCN)$ with a binuclear crystal structure classical for copper carboxylates.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.018.

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