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Syntheses and Crystal Structures of “Unligated” Copper(I) and Copper(II) Trifluoroacetates

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Two extremely unstable copper trifluoroacetates with no exogenous ligands, namely, $Cu(O_2CCF_3)$ (**1**) and $Cu(O_2CCF_3)_2$ (**2**), are prepared for the first time and obtained in crystalline form by deposition from the vapor phase. Their structures are determined by X-ray crystallography. The crystallographic parameters are as follows: for **1**, monoclinic space group $P2_1/c$, with $a = 9.7937(6)$ Å, $b = 15.322(1)$ Å, $c = 12.002(1)$ Å, $\beta = 106.493(9)°$, and $Z = 4$; for **2**, orthorhombic space group *Pcca*, with $a = 16.911(1)$ Å, $b = 10.5063(9)$ Å, $c = 9.0357(6)$ Å, and $Z = 4$. Both structures are unique among other Cu^I and Cu^{II} carboxylates, as well as among metal carboxylates in general. Compound **1** consists of a planar rhombus of four copper atoms with sides of 2.719(1)−2.833(1) Å and trifluoroacetate ligands bridging the pairs of adjacent metal atoms alternately above and below the plane. The tetrameric units are further aggregated in a polymeric zigzag ribbon $[Cu_4(O_2CCF_3)_4]_\infty$ by virtue of intermolecular Cu···O contacts. The structure of **2** is built on cis bis-bridged dimers in which every metal atom is also connected with two copper atoms of the neighboring units. The stacking planes in this extended chain are almost perpendicular to one another. The Cu···Cu distance inside the dimer is 3.086(2) Å, indicating a nonbonding interaction.

Introduction

There are several structural types of transition metal carboxylates known, for M^I and M^{II} ranging from bi- to tri-, tetra-, and even polynuclear species.[1] This structural diversity depends mainly on the coordination flexibility of metal ions and substituent groups on the carboxylic anions. For copper, both Cu^I and Cu^{II} carboxylates are well-known. Copper(I) compounds attract attention because of their involvement as intermediates in decarboxylation reactions of organic acids,[2] in the formation of esters from organic acids and alkyl halides,[3] in the preparation and reactions of olefin and alkyne complexes,[4] and as agents for the selective separation of certain aromatic hydrocarbons and promotion of their oxidation.[5] In Cu^{II} carboxylate chemistry, the study of the antiferromagnetic interactions propagated through the electronic orbitals of ligands bridging the metal centers has been the key point in a great deal of research.[6] In addition, some applications such as thin coatings against corrosion[7] and copper(II)-catalyzed oxidation of carboxylic acids[8] have been reported.

Since the unique and useful properties of copper carboxylates in general are connected to the molecular structure of the compounds, the question of the factors influencing structure variations commands attention. A large number of “unligated” (i.e., with no exogenous ligands) carboxylate complexes $Cu_2(O_2CR)_4$ have been reported,[7−9] all having the well-known polymeric structure **I** (Chart 1). The chemistry of copper(I) carboxylates has been relatively limited, and only $Cu_2(O_2CCH_3)_2$[10] and $Cu_4(O_2CC_6H_5)_4$[11] have been structurally characterized. The former consists of planar polymeric molecules (**II**) in which the $Cu_2(O_2CCH_3)_2$ molecules are linked into chains

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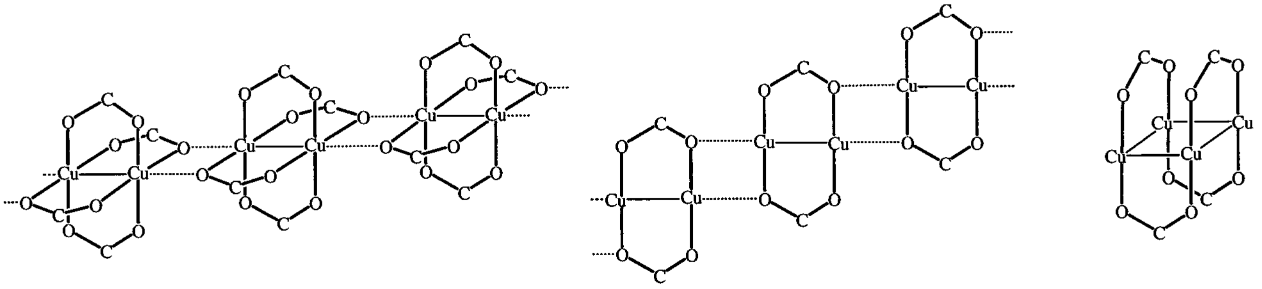
Chart 1. Structures of Copper Carboxylates without Exogenous Ligands: Dicopper(II) Tetracarboxylates, **I**; Copper(I) Acetate, **II**; (c) Copper(I) Benzoate, **III**



by further copper−axial oxygen interactions. The latter exhibits a tetrameric structure based on a parallelogram of Cu^I atoms with benzoate anions bridging the four metal pairs alternately above and below the plane (**III**).

Surprisingly, neither Cu^I nor Cu^{II} “unligated” trifluoroacetates have previously been reported, although some of their adducts are known. For copper(II) trifluoroacetate, there are two structures, both of the discrete bis-adduct type: $Cu_2(O_2CCF_3)_4(NC_9H_7)_2$[12] and $Cu_2(O_2CCF_3)_4(CH_3CN)_2$.[13] For copper(I) trifluoroacetate, two unusual tetranuclear adducts have been structurally characterized, namely, $Cu_4(O_2CCF_3)_4(C_6H_6)_2$[14] and $Cu_4(O_2CCF_3)_4(EtC{\equiv}CEt)_2$.[15]

It is known that the CF_3COO^- ligand exhibits the greatest “electron-withdrawing” ability of all carboxylates. This plus the coordination flexibility of copper atoms inspired us to prepare the structurally unknown “unligated” Cu^{II} and Cu^I trifluoroacetates with the expectation of finding unusual structural and chemical properties. It was a challenge to grow the crystals of these products and to handle them because of very high moisture sensitivity and the avidity of both compounds for additional coordination. We overcame these problems by using a solid-state sublimation technique,[16] which we have already proved to be a very efficient way to avoid the presence of exogenous ligands during crystal growth for rhodium(II) trifluoroacetate.[17] Special crystal-mounting procedures were also necessary (vide infra).

We succeeded in isolating both crystalline “unligated” $Cu(O_2CCF_3)$ (**1**) and $Cu(O_2CCF_3)_2$ (**2**). X-ray structures for **1** and **2** are presented here. When compared with those of other copper carboxylates, it is clear that both structures are absolutely unique. The effects on the Cu atoms of electron withdrawal by CF_3COO^- ligands with respect to their coordination spheres and the structural motifs in general are also discussed.

Results and Discussion

Synthetic Aspects. There are a number of reported high-yield preparations for a range of copper(I) carboxylates, $Cu(O_2CR)$ (R = H, CH_3, CF_3, C_2H_5, n-C_3H_7, C_6H_5, etc.).[10,11,18] It is worth mentioning that crystals of both of the structurally characterized “unligated” copper(I) carboxylates suitable for X-ray investigation were grown from solution: acetonitrile for $Cu(O_2CCH_3)$[10c] and xylene-containing benzoic acid for $Cu(O_2CC_6H_5)$.[11] Crystallization of copper(I) trifluoroacetate from even such a weakly coordinating solvent as benzene afforded crystals of the dibenzene adduct, $Cu_4(O_2CCF_3)_4(C_6H_6)_2$.[14] This made it evident that crystallization of the trifluoroacetate from solutions cannot in general be used for such an extremely powerful Lewis acid. Therefore, we first used the same literature procedure[14] for the preparation of copper(I) trifluoroacetate, which is based on the reaction of Cu_2O with trifluoroacetic anhydride in dry benzene at 60−70 °C, but then the benzene adduct of **1** was heated under vacuum for 24 h. This was followed by sublimation of the crude solid at 110−120 °C, which afforded crystals of **1** in good yield. Although it was mentioned that copper(I) acetate slowly disproportionates into copper(II) acetate and copper metal,[10b] sublimation of $Cu(O_2CCF_3)$ in our case proceeded cleanly, under the conditions used, to give only crystals of **1**. We also observed the sublimation of **1** even in a dynamic vacuum without decomposition at 120−130 °C and condensation of the product in the form of microcrystalline material. The question of what species may be present in the vapor is fascinating but remains unanswered.

Copper(II) carboxylates can be prepared by using standard literature procedures.[9a] Their crystals have been obtained from solutions in the corresponding carboxylic acids[9e,f,h] or in other solvents such as alcohol[9c] or xylene;[7] in some cases sublimation was successfully used for the preparation of crystalline “unligated” copper(II) compounds.[9e] As the ability of copper alkanecarboxylates to sublime was found to be extraordinary compared to that of other transition metal carboxylates, it appeared obvious for us to try deposition from the vapor phase to obtain crystals of the desired $Cu(O_2CCF_3)_2$ (**2**). The “unligated” copper(II) trifluoroacetate product was prepared from $Cu(O_2CCF_3)_2{\cdot}nH_2O$ by first replacing the water molecules with acetone, followed by removal of the acetone under mild heating at reduced pressure. Sublimation of the solid so obtained at 135−145 °C in an evacuated sealed tube always resulted in two types of crystals: blue needles of **2** (35−40%) and colorless

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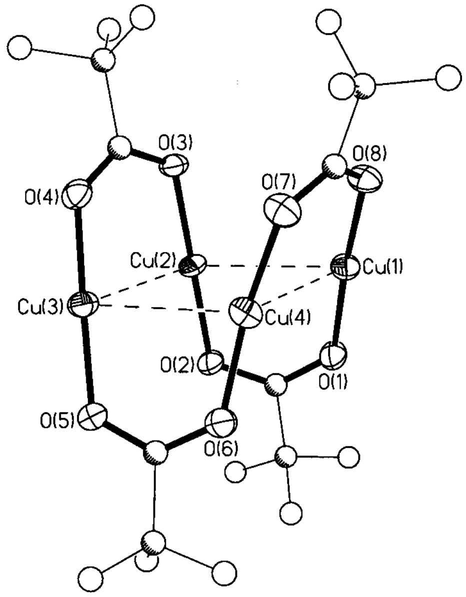

Figure 1. Perspective drawing of the $Cu_4(O_2CCF_3)_4$ tetramer in the crystal structure of copper(I) trifluoroacetate (**1**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and fluorine atoms are shown as spheres of arbitrary radii, with only one orientation of each disordered CF_3 group depicted. For clarity, only Cu and O atoms are labeled. The shortest Cu−Cu distances are indicated by dashed lines.

Table 1. Selected Distances (Å) and Angles (deg) in $[Cu_4(O_2CCF_3)_4]_\infty$ (**1**)

Cu(1)−Cu(2)	2.759(1)	Cu(1)−Cu(4)	2.819(1)
Cu(2)−Cu(3)	2.719(1)	Cu(3)−Cu(4)	2.833(1)
Cu(1)−O(1)	1.858(5)	Cu(3)−O(4)	1.850(6)
Cu(1)−O(8)	1.870(5)	Cu(3)−O(5)	1.878(5)
Cu(2)−O(2)	1.897(5)	Cu(4)−O(6)	1.858(6)
Cu(2)−O(3)	1.882(5)	Cu(4)−O(7)	1.868(6)
Cu(2)−Cu(1)−Cu(4)	64.46(4)	Cu(1)−Cu(2)−Cu(3)	118.21(4)
Cu(2)−Cu(3)−Cu(4)	64.78(4)	Cu(1)−Cu(4)−Cu(3)	112.52(4)
O(1)−Cu(1)−O(8)	174.1(3)	O(4)−Cu(3)−O(5)	175.5(3)
O(3)−Cu(2)−O(2)	177.8(2)	O(6)−Cu(4)−O(7)	164.1(3)
Cu(2)−Cu(1)−O(1)	78.8(2)	Cu(2)−Cu(3)−O(4)	81.5(2)
Cu(2)−Cu(1)−O(8)	105.4(2)	Cu(2)−Cu(3)−O(5)	100.0(2)
Cu(4)−Cu(1)−O(1)	96.1(2)	Cu(4)−Cu(3)−O(4)	94.0(2)
Cu(4)−Cu(1)−O(8)	82.3(2)	Cu(4)−Cu(3)−O(5)	82.9(2)
Cu(3)−Cu(2)−O(2)	98.2(2)	Cu(1)−Cu(4)−O(6)	108.6(2)
Cu(3)−Cu(2)−O(3)	83.5(2)	Cu(1)−Cu(4)−O(7)	79.9(2)
Cu(1)−Cu(2)−O(2)	84.8(2)	Cu(3)−Cu(4)−O(6)	79.0(2)
Cu(1)−Cu(2)−O(3)	95.7(2)	Cu(3)−Cu(4)−O(7)	110.8(2)

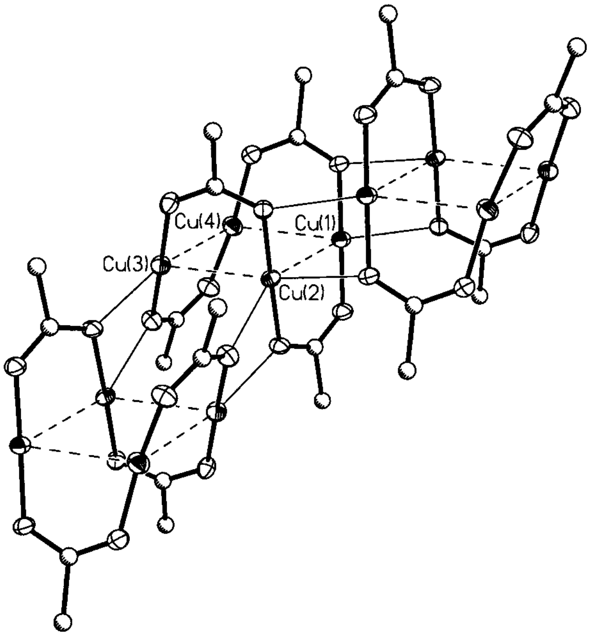

Figure 2. Arrangement of the $Cu_4(O_2CCF_3)_4$ tetrameric units in a fragment of the chain structure of **1**. Fluorine atoms of CF_3 groups are omitted for clarity. Four crystallographically independent Cu atoms are labeled. The shortest intermolecular Cu−O contacts are denoted by thin solid lines.

blocks of **1** (30−40%). At higher temperatures traces of Cu^0 were observed, which we suppose is the product of disproportionation reactions. Although we were unable to isolate any Cu^{III} product, mixed-valent Cu^{II}−Cu^{III} species have been identified in other deposition reactions.[19]

Compounds **1** and **2** are both extremely hygroscopic, rapidly absorbing moisture from the air or from incompletely dried glassware or solvent. It may be noted that the copper(II) product is less thermally stable and more avid for axial coordination than the copper(I) trifluoroacetate. Their facile reactions with water or any other solvent drastically restricted the handling and further investigation of both of these trifluoroacetate compounds. However, crystal structure determinations were successfully accomplished for both **1** and **2**.

Crystal Structures. Copper(I) Trifluoroacetate (1). For copper(I) trifluoroacetate, the main structural feature may be described as a planar rhombus of four crystallographically independent Cu atoms (Figure 1) with the Cu to Cu distances in the range 2.719(1)−2.833(1) Å. The interior angles are averaged to 115.37(4) and 64.62(4)°, and the short diagonal, Cu(2)⋯Cu(4), is 2.975(1) Å. The trifluoroacetate ligands bridge the four pairs of adjacent copper atoms around the tetramer in 1−2, 2−3, 3−4, and 4−1 fashions and are alternatively above and below the Cu_4 plane. The CO_2^- groups are almost perpendicular to the plane, with the O−Cu−O angles in the range 164.1(3)−177.8(2)° (Table 1).

The internal Cu−O distances are all very close and have an average value of 1.870(5) Å. In addition, however, three of the four copper atoms have intermolecular contacts with oxygen atoms of other tetrameric molecules (Figure 2). The Cu(1) and Cu(3) atoms each have one such contact at distances of 2.495(5) and 2.589(5) Å, respectively, while the Cu(2) atom displays two contact distances of 2.675(6) and 2.725(6) Å and an angle of 88.8(2)° between them. All these additional contacts are "axial" in relation to the rhombus edges, with the Cu−Cu−O angles varying from 156.5(1) to 165.8(1)°. These intermolecular interactions make the structure of copper(I) trifluoroacetate a polymeric zigzag-type ribbon.

The copper atoms in the structure of **1** display three different coordination types. With inclusion of the Cu⋯Cu contacts within the tetramer and of the Cu−O intermolecular interactions and by placement of the internal oxygen atoms in apical positions, the coordination polyhedra of the Cu(1) and Cu(3) centers can be regarded as highly distorted trigonal bipyramidal (Figure 3). The geometry around the Cu(2) atom can be viewed as tetragonally elongated octahedral, while the least "saturated" Cu(4) atom possesses a seesaw coordination.

Copper(I) trifluoroacetate is the third Cu(I) carboxylate whose structure has been elucidated, and all three structures are different. In the crystal structure of copper(I) acetate,[10,20] two Cu atoms (Cu−Cu distance is 2.548(2) Å) are bridged by two acetate groups, forming a planar eight-membered ring. These

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(19) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. Unpublished results.

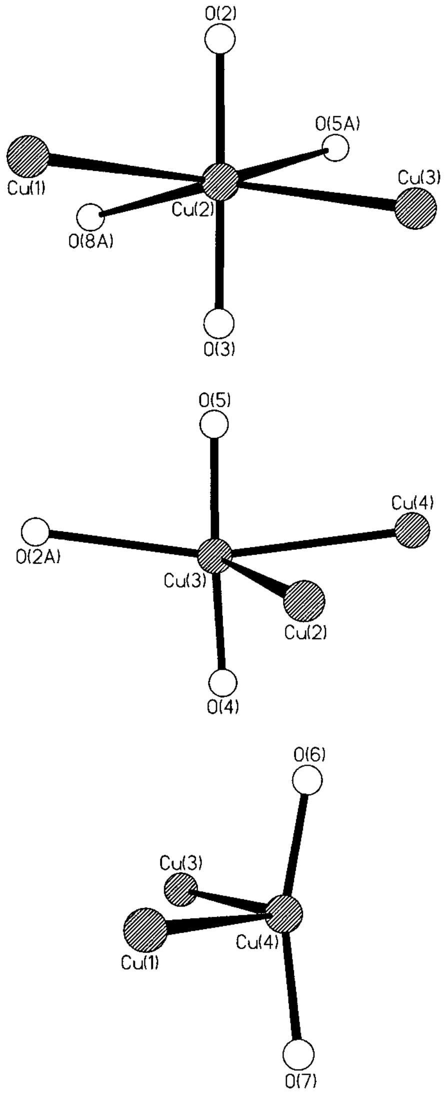

Figure 3. Three types of coordination polyhedra of Cu atoms in the crystal structure of copper(I) trifluoroacetate (**1**).

$Cu_2(O_2CCH_3)_2$ units are linked through two intermolecular Cu−O contacts (2.303(6) and 2.276(6) Å) to create a planar polymeric structure (Chart 2). An additional factor holding this motif together is hydrogen bonding between the H atoms of CH_3 groups and carboxylic oxygen atoms. In our structure refinement,[20] one of the hydrogen atoms was located in the same plane and directed toward the oxygen atoms, with an O···H separation of 2.6 Å and a C−H···O angle of 154°.

Chart 2. Three Structural Types of Cu^I Carboxylates: Copper(I) Acetate, Copper(I) Benzoate, and Copper(I) Trifluoroacetate

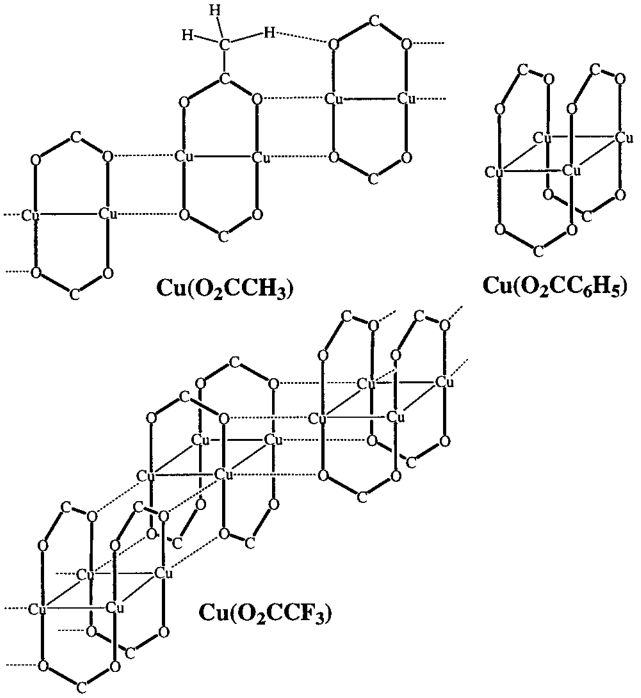

Table 2. Principal Distances (Å) and Angles (deg) for Three Types of Copper(I) Carboxylates (Chart 2)

	$Cu_2(O_2CCH_3)_2$[a]	$Cu_4(O_2CC_6H_5)_4$[b,c]		$Cu_4(O_2CCF_3)_4$ (**1**)[a]
Cu−Cu	2.548	2.709	2.732	2.759
		2.720	2.833	2.833
		2.756	2.719	2.719
		2.742	2.753	2.819
Cu−Cu−Cu		71.2	65.5	64.6
		108.8	114.5	115.4
Cu−O	1.90	1.84	1.84	1.87
O−Cu−O	170.6	173.9	173.4	172.9
Cu···O	2.30	3.04	3.08	2.50
Cu−Cu···O	164.0	158.5	128.5	165.8
	2.28	3.42	3.32	2.73
	163.1	168.8	157.3	156.5
		3.26	3.18	2.68
		174.6	163.3	156.6
		3.27	3.11	2.59
		138.8	172.8	164.2
Cu···Cu	3.235	3.236	3.313	3.330

[a] This work. [b] Reference 11. [c] For two crystallographically independent molecules.

The significance of C−H···O hydrogen bonding in the structure of copper(I) acetate becomes clear when we consider the structures of other carboxylates that have no β-hydrogen atoms. The structure of copper(I) benzoate[11] consists of tetrameric $Cu_4(O_2CC_6H_5)_4$ molecules (Chart 2) which are similar to those found in trifluoroacetate **1** (Table 2). The difference, however, is that the structure of the benzoate cannot be regarded as polymeric, since all intermolecular Cu···O contacts are much longer (3.04−3.42 Å) than those in the trifluoroacetate (2.50−2.73 Å). At the same time, the distances between tetramers (intermolecular Cu···Cu distances) are almost the same for both structures, namely about 3.3 Å. This implies that, in the trifluoroacetate, the Cu_4 planes are shifted up and down relative to each other (Chart 2) to provide short intermolecular contacts with carboxylate oxygen atoms of the neighboring units.

The coordination number of the copper atoms in both the acetate and benzoate structures is 4 with different geometries, planar and pyramidal, respectively. For the trifluoroacetate, however, the coordination number of the copper atoms is averaged to 5. Thus Cu^I atoms show a tendency to increase their coordination number when being ligated by strong electron-withdrawing groups such as CF_3COO^-. This ability has been manifested in the isolation of copper(I) trifluoroacetate adducts

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(20) Crystal data for $[Cu_2(O_2CCH_3)_2]_\infty$: monoclinic, $P2_1/m$ (*No.* 11), $a = 5.205(2)$ Å, $b = 6.166(2)$ Å, $c = 9.873(4)$ Å, $\beta = 93.58(3)°$, $V = 316.2(2)$ Å^3, $Z = 2$, $\rho_{calc} = 2.575$ g/cm^3, $T = 213$ K, full-matrix refinement on F^2 (Nonius FAST area detector, SHELXL-93), R1 (on F_o) = 0.0455, wR2 (on F_o^2) = 0.1346, GOF = 1.274 for 71 parameters and 12 restraints, 463 unique data (441 with $I > 2\sigma(I)$). See Table 2 for dimensions and the Supporting Information for other structure details.

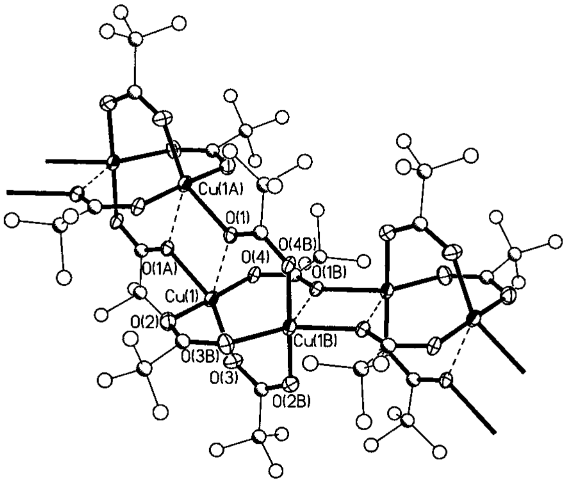
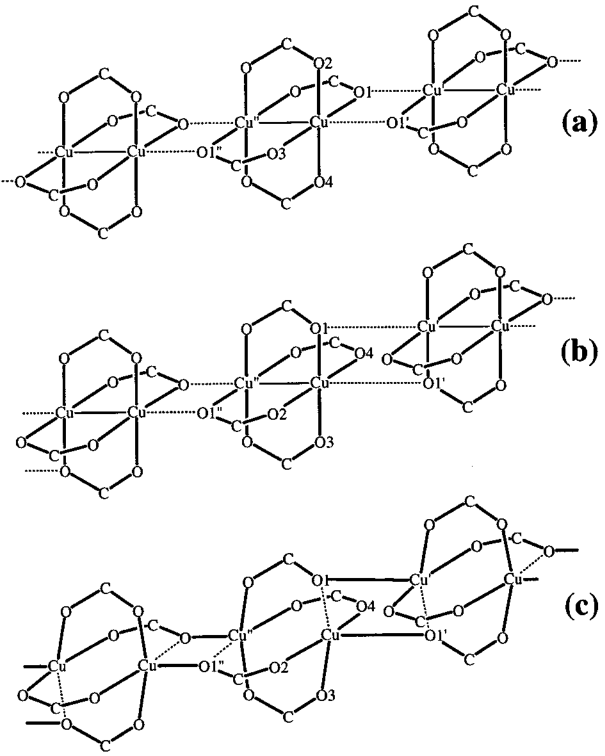


Figure 4. Fragment of the polymeric chain in the crystal structure of copper(II) trifluoroacetate (**2**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and fluorine atoms are shown as spheres of arbitrary radii, with only one orientation of each CF_3 group depicted. For clarity, only some Cu and O atoms are labeled. Long Cu−O contacts are depicted by dashed lines.

Table 3. Selected Distances (Å) and Angles (deg) in $[Cu_2(O_2CCF_3)_4]_\infty$ (**2**)

Cu(1)−Cu(1B)	3.086(2)	Cu(1)−O(4)	1.901(5)
Cu(1)−O(1)	2.419(5)	Cu(1)−O(1A)	2.054(5)
Cu(1)−O(2)	1.902(6)	O(1)−Cu(1A)	2.054(5)
Cu(1)−O(3)	1.963(6)		
O(1)−Cu(1)−O(2)	88.3(2)	O(2)−Cu(1)−O(3)	90.3(3)
O(1)−Cu(1)−O(3)	136.1(2)	O(2)−Cu(1)−O(4)	175.7(3)
O(1)−Cu(1)−O(4)	87.5(2)	O(3)−Cu(1)−O(4)	92.2(2)
O(1)−Cu(1)−O(1A)	76.6(2)	O(3)−Cu(1)−O(1A)	147.3(2)
O(2)−Cu(1)−O(1A)	90.5(2)	O(4)−Cu(1)−O(1A)	89.2(2)
Cu(1B)−Cu(1)−O(1)	67.4(1)	Cu(1B)−Cu(1)−O(4)	92.0(2)
Cu(1B)−Cu(1)−O(2)	85.7(2)	Cu(1B)−Cu(1)−O(1A)	143.8(2)
Cu(1B)−Cu(1)−O(3)	68.8(2)		
Cu(1)−O(1)−Cu(1A)	103.4(2)		

Chart 3. Three Structural Types of Cu^{II} Carboxylates: (a) Flat Ribbon; (b) “Venetian Blind”; (c) Copper(II) Trifluoroacetate



with such weakly coordinating ligands as benzene[14] and 3-hexyne.[15] The stoichiometry is the same for both complexes, $Cu_4(O_2CCF_3)_4L_2$ ($L = C_6H_6$, EtC≡CEt), and the tetrameric units are retained while the intermolecular interactions are lost upon ligand insertion. On the basis of the limited data available for the benzene adduct,[14] we may conclude that its core $Cu_4(O_2CCF_3)_4$ unit is very similar to the one found for the parent “unligated” compound. All copper atoms compensate for the loss of intermolecular Cu···O contacts by having long interactions (≥2.7 Å) with aromatic carbon centers. In the diethylacetylene (3-hexyne) adduct,[15] the geometry of the tetramer was found to be transformed from planar to distorted tetrahedral. In the resulting tetrahedron, the four long edges are spanned by trifluoroacetate groups, while two short edges are bridged by μ-EtC≡CEt ligands with short Cu−C distances of 1.92−2.00 Å. These two examples support the idea that, because of the cyclic bridged nature of the copper(I) trifluoroacetate (**1**) structure, the tetrameric unit is not easily broken upon exogenous ligand coordination. However, we have some preliminary indications that the $Cu_4(O_2CCF_3)_4$ units undergo cleavage under certain conditions, accompanied by a change in the oxidation state of the copper(I) atoms,[19] and study of this is continuing.

Crystal Structure of Copper(II) Trifluoroacetate (2). The crystal structure of copper(II) trifluoroacetate consists of infinite chains of dimers having the formal composition $Cu_2(O_2CCF_3)_4$ (Figure 4). All copper atoms in the chain are equivalent, since there are inversion centers between the units as well as a 2-fold axis passing through the center of each unit. Each dimer consists of two cis-located trifluoroacetate bridges with syn-syn geometry and Cu−O distances of 1.902(6) and 1.963(6) Å (Table 3). Each metal atom is also bridged to two other copper atoms from the neighboring dimers from left and right in a syn-anti and an anti-syn geometry with Cu−O contacts of 1.901(5) and 2.054(5) Å, respectively. Additionally, each copper atom has one more long contact with an oxygen atom of a trifluoroacetate group (2.419(5) Å) which is considerably longer than a normal Cu−O bond. The Cu···Cu distance inside the dimer is 3.086(2) Å, precluding any bonding interaction. Thus the coordination of the copper atoms in **2** may be regarded as highly distorted square pyramidal. The distance between metal atoms of neighboring dimers connected by a bridge of anti-syn geometry is 5.136 Å, and the closest Cu···Cu contact between two dimers via μ-O (carboxylate) bridges measures 3.518 Å.

Again, as in the case of copper(I) trifluoroacetate, the crystal structure of $[Cu_2(O_2CCF_3)_4]_\infty$ (**2**) has features which make it unique among all other Cu^{II} carboxylates. Most of the copper(II) carboxylates,[7−9] as well as an overwhelming majority of M^{II} carboxylates in general, have a paddlewheel tetrabridged structure of centrosymmetric dimers $Cu_2(O_2CR)_4$ which are further combined into infinite chains by pairs of Cu···O intermolecular bonds (Chart 3a). The intermolecular bonding involves trans carboxylate groups on each dimer so that the system of metal and bridging oxygen atoms constitutes a flat ribbon.

The Cu−Cu distances in the copper carboxylate dimers span the narrow range of 2.57−2.63 Å, and no dependence of the length on the substituent R of the carboxylate ligand has been found. The typical intramolecular Cu−O distance is about 1.94 Å, except for those of the oxygen atoms involved in linking interactions, which are about 0.05−0.07 Å longer. The inter-

Table 4. Principal Distances (Å), Angles (deg), Torsion Angles (deg), and Dihedral Angles (deg) for Three Types of Copper(II) Carboxylates

	$Cu_2(O_2CC_3H_7)_4$[a]	$Cu_2(O_2CC(CH_3)_3)_4$[b,c]	$Cu_2(O_2CCF_3)_4$[d]
Cu−Cu″ [e]	2.585	2.580	**3.086**
Cu−Cu′	3.260	3.310	**3.518**
Cu−O1	2.01	1.98	**2.42**
Cu−O2	1.94	1.94	1.90
Cu−O3	1.97	1.93	1.96
Cu−O4	1.94	1.94	1.90
Cu−O1′	**2.22**	**2.33**	**2.05**
Cu″−Cu−O1	82.8	90.0	**67.4**
Cu″−Cu−O2	83.9	88.7	85.7
Cu″−Cu−O3	86.6	80.7	**68.8**
Cu″−Cu−O4	85.6	78.0	92.0
Cu″−Cu−O1′	162.2	167.1	**143.8**
O1−Cu−O2	89.3	89.3	88.3
O1−Cu−O3	169.4	170.5	**136.1**
O1−Cu−O4	90.3	90.0	87.5
O2−Cu−O3	89.7	88.7	90.3
O2−Cu−O4	169.4	166.7	175.7
O3−Cu−O4	88.8	89.9	92.2
O1−Cu−O1′	79.4	79.8	76.6
O2−Cu−O1′	94.5	99.0	90.5
O3−Cu−O1′	111.2	109.7	**147.3**
O4−Cu−O1′	95.8	94.0	89.2
Cu−O1−Cu′	100.6	100.2	103.4
O1″−Cu″−Cu−O1	**180.0**	**84.1**	**86.2**
angle between stacking planes	**0.0**	**82.9**	**88.3**

[a] Reference 9b. [b] Reference 9d. [c] There is an error in 9d regarding the *x* coordinate of the O(8) atom in the structure of $Cu_2(O_2CC(CH_3)_3)_4$. For the data shown in Table 5, we assumed that coordinate to be 0.883 instead of the reported value of 0.833. [d] This work. [e] Numbering corresponds to the Chart 3.

molecular Cu−O bond is usually about 0.3 Å longer, in the range 2.22−2.28 Å, for different carboxylates.

Another structural variation for dicopper(II) tetracarboxylates was found[9e] for $Cu_2(O_2CC(CH_3)_3)_4$, and it is also characteristic for other pivalates of divalent metals such as chromium[21] and molybdenum.[22] In this structure, the intermolecular bonding involves two cis rather than trans carboxylate bridges of the $Cu_2(O_2CC(CH_3)_3)_4$, dimer (Chart 3b) and there is no inversion center. Such a structural pattern has been called a distorted "venetian blind". All dimensions for the crystal structure of $[Cu_2(O_2CC(CH_3)_3)_4]_\infty$ are similar to those for other copper(II) carboxylates, including Cu−Cu distances inside and between dimers (Table 4). The only real difference, apart from the consecutive bridging planes now being almost perpendicular to one another (82.9°), is in the intermolecular Cu···O contact which is about 0.1 Å longer for this type of stacking.

The structure of copper(II) trifluoroacetate can be regarded as a partially unzipped form of the pivalate type. This is because here (Chart 3c) again the noncentrosymmetric dimers are joined in nonplanar infinite chains with bridging planes lying at 88.3° relative to one another, but there are important differences between the two structures. We can visualize the transition from the structure of the pivalate to that of the trifluoroacetate as a matter of the copper atoms in the dimers moving apart, increasing the Cu···Cu distance by ~0.5 Å, toward oxygen atoms of neighboring units formerly involved in the intermolecular interaction. It is more difficult to recognize $Cu_2(O_2CCF_3)_4$ dimers in the polymeric chain, since they are bis-bridged now and each copper atom is also bridged with two other dimers.

This is quite the opposite of the situation for Cu^I carboxylates, where the high electron-withdrawing ability of trifluoroacetate ligands works toward an increase of the coordination number of the metal centers. In the case of copper(II) trifluoroacetate, the increase of Cu^{II} atom acidity leads to repulsion and reduction of the coordination number from 6 to 5 in comparison to the case of other carboxylates.

The fact that the pivalate and trifluoroacetate of copper(II), which have the most electronically diverse R groups among carboxylate anions, adopt linking patterns that are similar to each other but different from that found in all other copper(II) carboxylates is thought provoking. While we cannot offer an explanation, several observations may be pertinent. One is that the $C(CH_3)_3$ and CF_3 groups are sterically similar. Another is that they both lack β-hydrogen atoms. However, this may not be relevant in view of the structures of the tetrapropionate[6d,9b] and tetrabutyrate,[9c] neither of which has any hydrogen bonding in the direction of the chains. It is also possible that the structure in Chart 3b may be simply a high-temperature polymorph. It was shown recently for molybdenum(II) pivalate[23] that the structure in Chart 3a is obtained from solution while that in Chart 3b is found in crystals grown by sublimation.

On the basis of the stability and the solubility of copper(II) trifluoroacetate, we consider it a promising candidate for studying the interactions with very weak electron donors. As we have previously mentioned, two adducts of copper(II) trifluoroacetate are already known. They have a common discrete bis-adduct type of $Cu_2(O_2CCF_3)_4L_2$ structure where strong monodentate donors, quinoline[12] and acetonitrile,[13] occupy axial positions of the dimer. The dimers are tetrabridged, and the Cu−Cu distances are much shorter than in the corresponding "unligated" compound, being 2.886 and 2.766 Å, respectively. There is a clear indication of increased Lewis acidity of the Cu atoms in the trifluoroacetate compared to those in other copper(II) carboxylates. Thus, while the Cu−Cu

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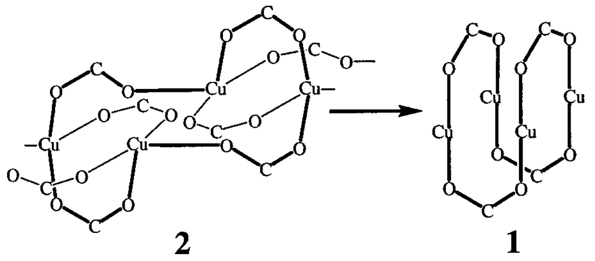
Scheme 1. Relation between the Structures of Copper(II) and Copper(I) Trifluoroacetates



distances in the acetate bis-adducts with quinoline[24] and acetonitrile[25] are about 0.13−0.23 Å shorter, the Cu−N distances are about 0.1 Å longer than those in the corresponding trifluoroacetate compounds.

It is interesting to think about the relation between the structures of the two copper trifluoroacetates, **1** and **2**, in connection with our observation that the copper(II) trifluoroacetate undergoes thermal decomposition (disproportionation?) to produce tetrameric $Cu_4(O_2CCF_3)_4$ molecules. Do such entities exist in the vapor phase? As can be seen from Scheme 1, this building block is already set in the structure of **2** and can be released upon reduction of the copper atoms and the loss of one trifluoroacetate ligand by each metal center.

Experimental Section

General Information. All the experimental manipulations involving the synthesis of the starting materials were carried out under dry, oxygen-free argon by employing Schlenk techniques. Starting materials, $Cu_2(O_2CCF_3)_4 \cdot nH_2O$, Cu_2O, and $(CF_3CO)_2O$, were purchased from Aldrich. The EI/DP mass spectra were acquired at 10−70 eV using a VG Analytical 70S high-resolution, double-focusing, sectored (EB) mass spectrometer. Elemental analyses were performed by Canadian Microanalytical Services, Ltd.

Preparation of $Cu(O_2CCF_3)$ (1). To Cu_2O (0.451 g, 3.15 mmol) was added 2 mL of $(CF_3CO)_2O$, followed by 30 mL of benzene. The mixture was refluxed overnight to give a blue solution and some unreacted red solid. This suspension was filtered through Celite to remove the Cu_2O. The blue solution was then evaporated to dryness, affording a very pale blue solid. This was heated at 60−70 °C under vacuum for 10−15 h to give “unligated”copper(I) trifluoroacetate (**1**). Yield: 0.710 g (64%). Anal. Calcd for $Cu_4C_8O_8F_{12}$: C, 13.60; F, 32.28. Found: C, 13.44; F, 31.74. MS (EI/DP; 10−70 eV scan; *m*/*z*): 242 $[Cu_2(O_2CCF_3)^+]$. Crystals of **1** as large transparent blocks were obtained by sublimation of the crude solid in a sealed evacuated tube at 110−120 °C for 2−3 days.

Preparation of $Cu(O_2CCF_3)_2$ (2). $Cu(O_2CCF_3)_2 \cdot nH_2O$ (0.561 g, 1.94 mmol) was dissolved in 3 mL of acetone to give an intensely blue suspension. Filtration and removal of all volatiles under reduced pressure afforded a blue-green residue, which was kept under a dynamic vacuum at 70−80 °C for 34 h to give a green solid. Yield: 0.489 g (87.2%). Anal. Calcd for $Cu_2C_8O_8F_{12}$: C, 16.59; F, 39.37. Found: C, 16.38; F, 39.07. MS (EI/DP; 10−70 eV scan; *m*/*z*): 351 $[Cu_2(O_2CCF_3)_2^+]$, 242 $[Cu_2(O_2CCF_3)^+]$. Sublimation of the crude solid in an evacuated sealed ampule at 135−145 °C for 3 days yielded two types of crystals: light-blue needles and transparent blocks. The latter were identified by X-ray diffraction to be identical to **1**, while the former were shown to be copper(II) trifluoroacetate (**2**). Some polycrystalline unidentified material in the form of bluish whiskers was also present.

Table 5. Crystallographic Data for $[Cu_4(O_2CCF_3)_4]_\infty$ (**1**) and $[Cu_2(O_2CCF_3)_4]_\infty$ (**2**)

	1	**2**
empirical formula	$Cu_4O_8C_8F_{12}$	$Cu_2O_8C_8F_{12}$
fw	706.24	579.16
space group	$P2_1/c$ (No. 14)	*Pcca* (No. 54)
a, Å	9.7937(6)	16.911(1)
b, Å	15.322(1)	10.5063(9)
c, Å	12.002(1)	9.0357(6)
β, deg	106.493(9)	
V, Å^3	1726.9(2)	1605.4(2)
Z	4	4
ρ_{calcd}, g cm^{-3}	2.716	2.396
μ, mm^{-1}	5.024	2.823
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	−60	−60
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0574, 0.1557	0.0616, 0.1458
R1,[a] wR2[b] (all data)	0.0642, 0.1649	0.0681, 0.1524

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

X-ray Structure Determinations. Single crystals of compounds **1** and **2** were obtained as described above. X-ray diffraction experiments were carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. Details concerning data collection have been fully described elsewhere.[26] The ampules were opened in an argon drybox, and crystals were quickly mounted with silicone grease on the tips of quartz fibers that were already connected to the goniometer head. Each setup, placed in a rigid plastic container, was then moved to the diffractometer and affixed in a cold N_2 stream (−60 °C) provided by a low-temperature controller. The total time during which each crystal was exposed to the atmosphere did not exceed 10 s.

Fifty reflections were used in cell indexing and 250 reflections in cell refinement. Axial images were used to confirm the Laue group and all dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.[27] Reflection profiles were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[28] The intensities were also corrected for anisotropy effects using a local adaptation of the program SORTAV.[29]

All calculations were done on a DEC Alpha computer running VMS. The coordinates of copper atoms for the structures were found in direct method *E* maps using the structure solution program SHELXTL.[30] The remaining atoms were located after an alternating series of least-squares cycles and difference Fourier maps.[31] The fluorine atoms of all CF_3 groups were found to be disordered over three different rotational orientations. Anisotropic displacement parameters were assigned to all atoms,

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except the disordered fluorine atoms. Relevant crystallographic data for complexes **1** and **2** are summarized in Table 5.

We also redetermined the crystal structure of copper(I) acetate[20] obtained by the "high-temperature" technique to see if it is of the same form as the crystals obtained from solution at room temperature.[10] The two structures were found to be the same, but the results of our determination are more precise than those reported earlier.[10] The new data can be found in the Supporting Information.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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