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Hydrothermal Synthesis of a Dense Metal−Organic Layered Framework That Contains Cu(I)−Olefinic Bonds, $Cu_2(O_2CCH{=}CHCO_2)$

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In recent years, controlled self-assembly of materials via low-temperature routes has gained importance due to its wide breadth of application toward advanced materials. These materials include zeolites, microporous materials, molecular magnets, and polymeric inorganic/organic frameworks.[1−14] Crystal engineering strategies involve consideration of the functionality of the building blocks, symmetry of the ligands, covalent bonding, hydrogen bonding, and metal−ligand coordination environments. It is well established that porous materials can be produced with these strategies. Interestingly, we have discovered that dense inorganic polymeric phases that exhibit unusual coordination to transition-metal centers can also be achieved with hydrothermal methods. We report the hydrothermal synthesis of an air-stable, unhydrated, densely layered, Cu(I) compound in which the Cu geometry is trigonal planar, and coordinated in organometallic fashion to an alkene substituent. In addition to the interesting coordination around Cu, this material is one of only few examples of trigonal planar Cu(I) in an extended solid framework.[15−18]

The title phase was synthesized by dissolving $Cu(CH_3CO_2)_2 \cdot H_2O$ (Aldrich) and fumaric acid (*trans*-$HO_2CCH{=}CHCO_2H$, Aldrich) in a 1:2 ratio in 7 mL of distilled water. The mixture was placed in a 23 mL Teflon-lined autoclave (Parr bomb), sealed, and placed in a furnace at 155 °C for 1.5 days. Orange needlelike crystals up to 1 mm in length were isolated from a clear solution (pH = 2−4), washed with distilled water, and air-dried. The yield of crystalline material was 60% based on $Cu(CH_3CO_2)_2$, and the synthesis was highly reproducible. EPR measurements were taken on single crystals, and the data confirmed that only Cu(I) was present. The orange color is not inconsistent with Cu(I) compounds since, for example, crystals of Cu_2O are red. Single crystals of $Cu_2(O_2CCH{=}CHCO_2)$ were ground in KBr, pressed into a pellet, and FTIR data were acquired (cm^{-1}): 3047(w), 1521(s), 1388(s), 1353(s), 1212(m), 1194(m), 776(w), 711(w). Additional evidence of the stability of the $Cu_2(O_2CCH{=}CHCO_2)$ compound was obtained by a melting point analysis of crystals, which only exhibited color darkening at 300 °C with no other evidence of decomposition or melting up to 360 °C.

Single-crystal X-ray diffraction[19] data obtained on a Siemens SMART CCD-area detector based diffractometer yielded a complicated layered structure as shown in Figure 1. Each layer is comprised of parallel copper fumarate chains that are linked in two directions forming a triple tier copper fumarate network. The first and third tier are symmetry-equivalent. Each tier contains eight-membered rings that contain O−Cu−O bonds (Figure 2), and the copper atoms are also bonded to ethylene substituents of neighboring chains (above the plane of the rings), forming trigonal planar centers. There is a gap of approximately 3.0 Å between the neighboring three-tiered layers along the *c*-axis direction.

There are four unique crystallographic entities in this structure, and all of them involve the Cu centers. The copper centers are Cu(1), Cu(2), Cu(3a), and Cu(3b) (Figure 2). Each of the copper centers are bonded to fumarate, and there are two unique fumarate molecules in the unit cell.

The Cu(1) coordination sphere is a pseudo trigonal pyramid. Cu(1) is located in the center tier of the layer and is bonded to O(5) and O(6) with Cu−O distances of 1.987(5) and 2.027(5) Å, respectively. Cu(1) is also bonded to an olefinic C=C group with nearly equivalent distances to C(2) and C(3) of 2.039(8) and 2.057(7) Å, respectively. The Cu(1) atom is at the center of a triangle formed by the O(5) and O(6) atoms and the middle of the ethylene group C(2)=C(3). Since Cu(1) is 2.335(5) Å from O(6′) of the next chain in the same plane, Cu(1)−O(6′) may be considered a fourth bond to Cu(1), thereby forming a pseudo trigonal pyramid. However, Cu(1)−O(6′) is likely a weak interaction, similar to those found in other Cu(I)−O-containing organometallic complexes.[20] The double bond between C(2) and C(3) of 1.488(9) Å is elongated relative to that of free ethylene (1.34 Å). The lengthening of the C=C distance is typical for ethylene that is η^2-bonded to low-valent, electron-rich, transition metals.[21]

The Cu(2) center is trigonal planar in coordination, but it is not bonded to an olefinic group as is Cu(1). Instead, Cu(2) is coordinated to three oxygen atoms, forming a planar "T" shape. The Cu(2) bond lengths to O(1), O(3), and O(4) are 1.909(5), 1.887(5), and 2.231(5) Å, respectively. Furthermore, Cu(2) achieves a square planar coordination sphere when it is also bonded to Cu(3b) (50% occupied). When Cu(3b) is present, it is 2.535(5) Å from Cu(2). The Cu−Cu distance is slightly shorter than bond lengths observed for Cu metal (2.556 Å). This square planar geometry of Cu(2) is nearly identical to what is observed for copper atoms in Cu(I) acetate.[22]

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(19) For $Cu_2(O_2CCH{=}CHCO_2)$: fw 241.13, $a = 5.1085(2)$, $b = 8.4464(4)$, and $c = 9.0987(2)$ Å, $\alpha = 98.298(2)°$, $\beta = 96.627(2)°$, $\gamma = 104.739(2)°$, $V = 370.92(3)$ Å^3, $Z = 3$, space group = $P1$, $T = 298$ K, $\lambda = 0.710\,73$, $\rho_{calcd} = 3.24$ g cm^{-3}, $\mu = 85.2$ cm^{-1}, transmission coeff = 0.55−0.84, R1 = 0.055, wR2 = 0.142

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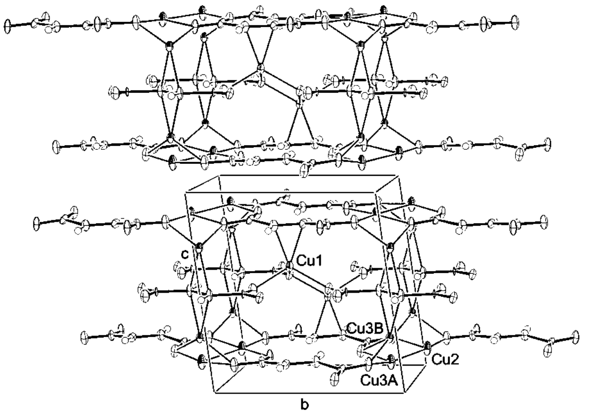

Figure 1. Perspective view normal to the bc plane of the unit cell of $\mathrm{Cu_2(O_2CCH{=}CHCO_2)}$ showing the triple layer packing. Thermal displacement ellipsoids are drawn at the 30% probability level except for hydrogen atoms, which are shown as spheres with an arbitrary size. Copper atom ellipsoids are drawn with octant shading and are labeled.

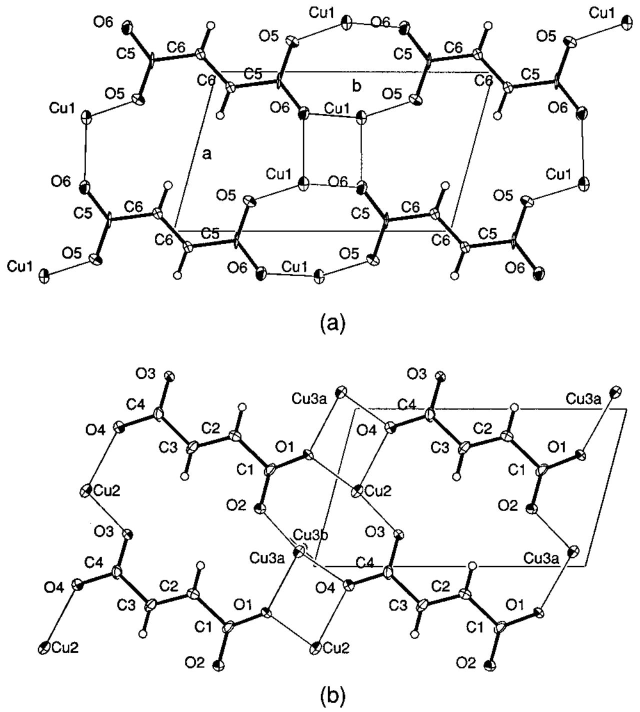

Figure 2. The two crystallographically independent layers at $z \approx {}^1/_2$ and $z \approx {}^1/_6$ in $\mathrm{Cu_2(O_2CCH{=}CHCO_2)}$ are shown in a and b, respectively.

Cu(3) was modeled with two sites, Cu(3a) and Cu(3b), which are 1.149(3) Å apart with refined occupancies of 0.505(5) and 0.496(5), respectively. Cu(3a) is similar in coordination to Cu(1), and Cu(3b) is similar to Cu(2).

Thus, the Cu(3a) coordination is described again as a pseudo trigonal pyramid with two short Cu−O distances, Cu(3a)−O(2) = 2.058(6) Å and Cu(3a)−O(4) = 2.120(6) Å, and with a longer Cu(3a)−O(1) distance of 2.303(5) Å. Cu(3a) is also coordinated to an olefinic substituent in which the Cu(3a) to C(6) and C(6′) distances are 2.160(3) and 2.173(8) Å, respectively. The C(6)=C(6′) double bond distance of 1.371(14) Å is slightly longer than C=C of free ethylene (1.337(2) Å). This is similar to other examples of organometallic complexes of Cu(I) bonded to an ethylene group in which the C=C bond is only slightly longer than that of free ethylene.[20,23,24] The olefinic bond here is not as elongated as compared to C(2)=C(3) (1.488(9) Å, bonded to Cu(1)), and this may be attributed to the Cu(3a) site only being 50% occupied.

Cu(3b) is distorted square planar with bonds to three oxygen atoms O(1), O(2), and O(4) with distances of 2.306(5), 1.833(6), and 1.866(5) Å, respectively, and bonded to Cu(2) at a distance of 2.535(5) Å.

Clearly, the mild conditions of hydrothermal synthesis provides an opportunity to obtain new solid state compounds in which unusual oxidation states and coordination spheres are achieved. Since reported examples of Cu(I) in either pseudo trigonal pyramidal or trigonal planar geometry in an extended structure are quite rare, $\mathrm{Cu_2(O_2CCH{=}CHCO_2)}$ is extraordinary with its multiple unique crystallographic Cu(I) trigonal planar centers. Indeed it is surprising that this dense (ρ = 3.24 g cm^{-3}) copper fumarate compound was synthesized under such mild conditions, especially when a microporous phase was expected. A unique and dominant character of the $\mathrm{Cu_2(O_2CCH{=}CHCO_2)}$ phase is that Cu(I) is also bonded to a C=C π-system to form densely packed layers, and thus the compound exhibits classical and nonclassical Cu(I) bonding. The stabilization of Cu(I) bonded to olefin is due to the high concentration of bonding, thereby allowing the title phase to be air-stable. The classical (Cu−O) bonding constrains the fumarate anions to be rigidly incorporated into the lattice and thus prevents any oxygen or water molecules to insert into the copper−olefin bond. There exist many structures in which Cu(I) is bonded to ethylene, but those are typically air-sensitive organometallic compounds that are molecular in nature where the olefin ligand is linked to the Cu(I) center only by the η^2-bond.[23−26] The molecular organometallic Cu(I)−ethylene compounds tend to be air-sensitive due to the loss of the ethylene substituent. In addition, the title phase curiously excludes water from the framework, and yet it was hydrothermally synthesized. In this case, the absence of waters of hydration appear to be due to the absence of voids and the saturation of the copper coordination by the fumarate ions. By far, most compounds obtained using this method contain water, and thus $\mathrm{Cu_2(O_2CCH{=}CHCO_2)}$ is a further example of using hydrothermal synthesis as an exploratory route to new phases.

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Supporting Information Available: A figure showing the unit cell (1 page). Details of the crystal structure determination, positional and thermal parameters, bond lengths and angles, in CIF format, are available through the Web only. See any current masthead page for ordering information and Web access instructions.

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