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Communication

Vapor-Diffusion-Mediated Single Crystal-to-Single Crystal Transformation of a Discrete Dimeric Copper(II) Complex to a Discrete Tetrameric Copper(II) Complex

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The symmetric dimeric complex $[Cu(\mu_2\text{-hep})(TFA)(H_2O)]_2$ (**1**) has been synthesized from 2-(2-hydroxyethyl)pyridine (hep-H), trifluoroacetic acid (TFA-H), and copper acetate in a 95:5 (v/v) MeOH−H_2O mixture at 298 K. Each Cu^{II} ion in **1** is linked with two μ_2-alcoholic oxygen atoms and one pyridine nitrogen atom of hep, and the other two coordination sites are occupied by the oxygen donors of TFA and H_2O. At room temperature, the *blue* single crystals of **1** transform to the *green* single crystals of a tetrameric complex, $[Cu_4(\mu_3\text{-hep})_2(\mu_2\text{-hep})_2(\mu_2\text{-TFA})_2(TFA)_2]$ (**2**), in presence of alcoholic vapor. The facile single crystal-to-single crystal (SCSC) transformation of **1** to **2** is accompanied by the removal of coordinated H_2O molecules in **1** and concomitant formation of four new covalent bonds, two Cu−O(μ_3-hep) and two Cu−O(μ_2-TFA). The SCSC transformation of **1** to **2** is selective to the alcoholic vapor; the exposure of single crystals of **1** to heat or light or in vacuum has resulted in an immediate loss in crystallinity.

The transformation of discrete or polymeric molecular frameworks at the single crystal-to-single crystal (SCSC) level is a fast-emerging topic in chemical sciences.[1] Such a phenomenon has potential applications in catalysis,[2a,2b] magnetism,[2c,2d] and the design of sensing devices.[2e,2f] The SCSC transformation, which retains crystallinity, can primarily be achieved via the influence of either temperature or light or by a simple vapor-diffusion technique. Although SCSC transformations by the aid of heat[3] or light[4] are known, to the best of our knowledge, there exist only two examples of nonporous gas−solid-mediated SCSC transformation.[5] One is a reversible exchange of a coordinated solvent molecule in a trinuclear iron complex from water to methanol to water at room temperature without changing the structural motif,[5a] and the second is an irreversible SCSC transformation from a trimeric copper complex to its monomeric analogue.[5b] In the latter case, the single crystals in the mother liquor were used for the vapor-diffusion process. Heat- and light-mediated SCSC transformations involving coordination polymers and networks of cadmium, nickel, manganese, and cobalt with special emphasis on molecular helicity, structural integrity, and magnetism have been reported recently.[6,7]

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In this Communication, we report a unique example of the facile SCSC transformation of a discrete dimeric copper(II) complex, $[Cu(\mu_2\text{-hep})(TFA)(H_2O)]_2$ (**1**), to a discrete tetrameric copper(II) complex, $[Cu_4(\mu_3\text{-hep})_2(\mu_2\text{-hep})_2(\mu_2\text{-TFA})_2(TFA)_2]$ (**2**; hep-H = 2-(2-hydroxyethyl)pyridine and TFA-H = trifluoroacetic acid) by the application of a simple vapor-diffusion technique at room temperature (Scheme 1 and the Supporting Information, SI).

In general, solvent-vapor-mediated transformation of crystal structures are not unusual, as is observed in many complexes showing vaporchromism behavior,[1f,5,8] in which the solvent molecules are trapped in the crystal. However, in the present case, the alcoholic vapor assists the removal of H_2O molecules from the crystal of **1**, leading to an unprecedented and interesting SCSC transformation.

The dimeric complex **1** has been synthesized by the reaction of hep-H and TFA-H with a methanolic solution [95:5 (v/v) MeOH−H_2O mixture] of copper acetate at room temperature for 6 h (SI). The use of pure water or dry methanol did not yield any **1**.

The solid-state structure of **1** (Tables S1 and S2 in the SI) has been confirmed by single-crystal X-ray diffraction studies[9] (Figure 1).

1 crystallizes in the monoclinic $C2/c$ space group with a crystallographically imposed inversion center. Both Cu^{II} ions are in a symmetric pentacoordinated (CuO4N) environment, firmly bound by two μ_2-alcoholic oxygen atoms and one pyridine nitrogen atom of hep; the remaining two coordination sites at each copper ion are occupied by the oxygen donors of acetate (TFA) and H_2O molecules.

The core structure is further stabilized by the formation of a central four-membered planar Cu_2O_2 ring (Figure 1). Three Cu−O bond distances are observed: Cu1−O1 1.933(3) Å; Cu1−O2 1.951(3) Å; Cu1−O4 2.290(3) Å. The axial position is occupied by the O4 atom of the H_2O molecule with an elongated Cu1−O4 distance, resulting in a distorted square-pyramidal geometry with built-in Jahn−Teller distortion. The copper ions in **1** are separated by 3.047 Å.

Moreover, the hydrogen atoms of the coordinated H_2O molecules in **1** form moderately strong hydrogen bonds[10] (H···O = 1.958−2.102 Å; O−H···O = 170−172°) with the acceptor oxygen atoms of the free carbonyl group of TFA and hep, leading to the formation of a tetrameric cluster core, as shown in Figure 2 (Table S3 and Figure S1 in the SI).

The formation of such a hydrogen-bonded tetrameric feature via interactions between the coordinated solvent H_2O molecules and the ligands hep/TFA in the crystal

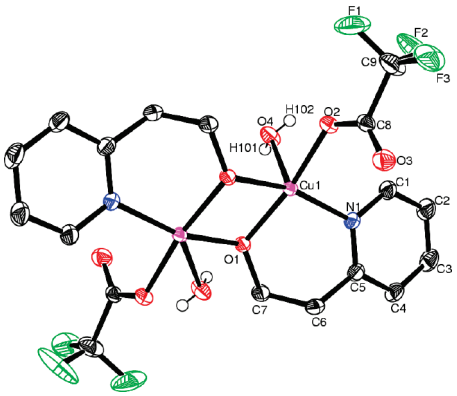


Figure 1. Thermal ellipsoid plot of **1** with 50% probability.

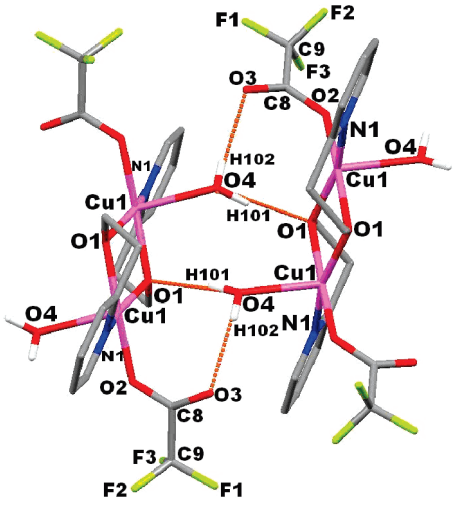
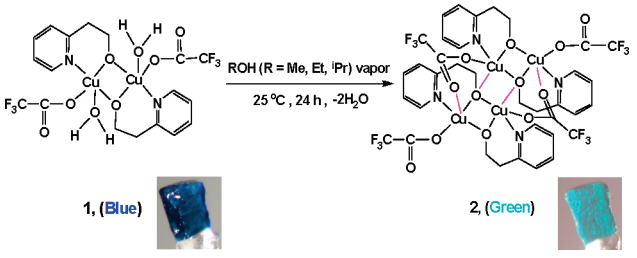


Figure 2. Hydrogen-bonded tetrameric feature of **1**.

Scheme 1. SCSC Transformation of **1** (*Blue* Crystals) to **2** (*Green* Crystals)



structure of **1** (Figure 2) prompted us to explore the effect of exposing **1** to the vapors of alcohols, ROH (R = Me, Et, ^{i}Pr). Upon exposure of the blue single crystals of **1** to various alcohols (Figure S2 in the SI), the color of the crystals changed to green. The subsequent structural analysis of the resultant green crystals reveals its identity as a tetrameric copper complex **2** (Figure 3).

Attempts to synthesize **2** independently from the powdered bulk sample of **1** in dry alcohol or acetonitrile, however, failed altogether (see the SI). Moreover, under the vapor-diffusion process, the expected direct exchange of a coordinated H_2O molecule in the single crystal of **1** by CH_3OH, as has been reported in the case of trinuclear $[Fe_3(\mu_3\text{-O})(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]ClO_4\cdot 3H_2O \rightleftharpoons Fe_3(\mu_3\text{-O})(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(MeOH)]ClO_4\cdot 3H_2O$,[5a] did not take

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(9) Crystal data for **1**: $C_{18}H_{20}N_2O_8F_6Cu_2$, M = 633.44, monoclinic $C2/c$, Z = 4, T = 150(2) K, $F(000)$ = 1272, a = 13.89(2) Å, b = 15.8882(12) Å, c = 10.763(12) Å, β = 97.85(16)°, V = 2352(5) Å^3, D_c = 1.789 mg/m^{-3}, μ(Mo Kα) = 1.902 mm^{-1}, size = 0.34 × 0.30 × 0.28 mm^3, GOF = 1.102, rflections collected/unique, 6630/2076 [R(int) = 0.0165], R1 [$I > 2\sigma(I)$] = 0.0232, wR2 = 0.0571, R indices (all data) R1 = 0.0271, wR2 = 0.0586. Crystal data for **2**: $C_{36}H_{32}N_4O_{12}F_{12}Cu_4$, M = 1194.83, monoclinic, $P2_1/n$, Z = 2, T = 150(2) K, $F(000)$ = 1192, a = 8.5271(14) Å, b = 21.778(4) Å, c = 11.465(2) Å, β = 90.710(17)°, V = 2129.0(7) Å^3, D_c = 1.864 mg/m^{-3}, μ(Mo Kα) = 2.089 mm^{-1}, size = 0.32 × 0.28 × 0.25 mm^3, GOF = 0.891, reflections collected/unique, 18 744/3740 [R(int) = 0.1470], R1 [$I > 2\sigma(I)$] = 0.0501, wR2 = 0.0772, R indices (all data) R1 = 0.1115, wR2 = 0.0921. CCDC CIF deposition numbers: 661087 and 701543 for **1** and **2**, respectively.

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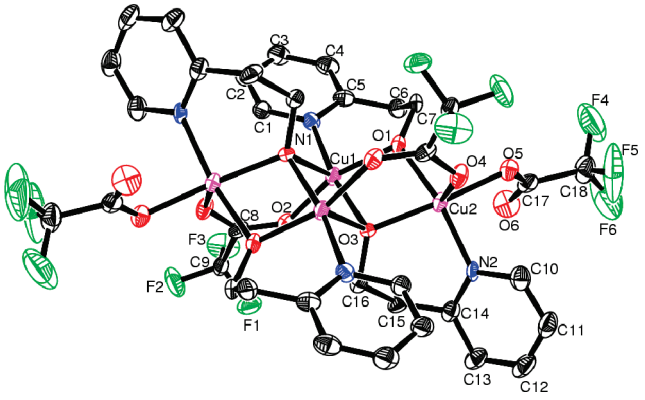

Figure 3. Thermal ellipsoid plot of **2** with 50% probability.

place. This is most likely because of the faster rate of coordination of the suitably configured pendent carbonyl function (−C═O) of the bonded TFA (anti to the H_2O molecule) in **1** than that of the external MeOH from the vapor to the vacant Cu centers developed by the removal of coordinated H_2O molecules in the neighboring two dimeric **1** (Scheme 1). This indeed led to the irreversible formation of the tetrameric core of **2**.

2 possesses a monoclinic $P2_1/n$ space group with a crystallographically imposed inversion center (Tables S1 and S2 in the SI). The SCSC transformation of **1** to **2** via the removal of coordinated H_2O molecules in **1** is found to be selective with protic alcoholic solvents such as methanol, ethanol, or isopropyl alcohol. No such transformation was found to take place with nonprotic solvents such as *N*,*N*-dimethylformamide, dimethyl sulfoxide, or tetrahydrofuran even at higher temperatures. However, partial conversion of **1** to **2** has been observed in acetonitrile but with a loss in crystallinity. Single crystals of **1** are found to be stable at ambient conditions. Exposure of **1** to heat, light, or vacuum resulted in green **2** but with *immediate loss in crystallinity*.

The SCSC transformation of **1** to **2** is accompanied by the breaking of Cu−O(H_2O) bonds in **1**. Concomitant formation of four new covalent bonds, two Cu−O(μ_3-hep) and two Cu−O(μ_2-TFA) (Scheme 1), prevents the backward SCSC process of **2** to **1** upon exposure of the crystals of **2** to the water vapor.

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The tetranuclear copper(II) complex, **2**, is composed of four monoanionic hep and four trifluoroacetate ligands. The central Cu_4O_4 unit in **2** is arranged in a chair-like conformation (Figure S3 in the SI), as has been observed earlier in hydroxy-bridged copper tetramer $\{[Cu(bpy)(OH)]_4Cl_2\}$-$Cl_2 \cdot 6H_2O$.[11] The Cu1 atom in **2** exhibits square-pyramidal geometry (4 + 1): one nitrogen atom from hep, two oxygen atoms from μ_3-hep, one oxygen atom from μ_2-hep, and one oxygen atom from μ_2-TFA. The Cu2 ion in **2** also exhibits square-pyramidal geometry (4 + 1) with a different coordination mode: one nitrogen atom from hep, one oxygen atom from μ_3-hep, one oxygen atom from μ_2-hep, one oxygen atom from μ_2-TFA, and one oxygen atom from monodentate TFA. The Cu−N distances in **2** vary slightly; however, reasonable variations in the Cu−O distances are observed depending on their connectivities (Table S2 in the SI). If the weak interactions are ignored, the transformation of **1** to **2** is a 0D-to-0D structural transformation (Figure S4 in the SI). In the SCSC transformation of **1** to **2**, alcohol plays a significant role in removing the coordinated H_2O molecule from **1**, which, in turn, facilitates the formation of new Cu−O covalent bonds in **2**. The IR spectrum of **2** is similar to that of **1** except that the O−H vibration of coordinated H_2O molecules in **1** is absent in **2** (Figure S5 in the SI). In addition, the TGA of **1** under N_2 reveals a weight loss of ∼4% in the temperature range of 50−120 °C corresponding to the loss of two coordinated H_2O molecules, whereas no such weight loss in TGA was detected for **2** up to 150 °C (Figure S6 in the SI).

In conclusion, the present work demonstrates a unique example of a facile gas−solid-mediated SCSC transformation of a discrete dimeric copper(II) complex (**1** = *blue* crystal) to a discrete tetrameric copper(II) complex (**2** = *green* crystal) via the removal of coordinated H_2O molecules in **1** and concomitant formations of new μ_2-O (TFA) and μ_3-O (hep) covalent bonds with Cu in **2**. The SCSC transformation of **1** to **2** is selective in protic alcoholic solvents. The observed significant structural changes in moving from **1** to **2** at the SCSC level can be considered as a promising synthon toward the design of newer classes of versatile multifunctional crystalline materials.

Supporting Information Available: Experimental procedures and structural and spectral details of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.