Studies of the Mechanism of a Single-Crystal-to-Single-Crystal Reversible Dehydration of a Copper Carboxylate Framework

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The open-framework copper carboxylate chloride $[Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)_2](H_2O)_4$ (THFTC = tetrahydrofuran-2,3,4,5-tetracarboxylate) was synthesized hydrothermally and was characterized structurally and magnetically. The centrosymmetric three-dimensional framework has channels filled with water. Single crystals kept under vacuum at different temperatures (room temperature, 65 °C, and 105 °C) remain single while the structure is dehydrated in steps accompanied by distortions of the framework and repositioning of the water molecules and chlorine atoms. The dehydrated compounds are acentric and have two distinct channels with different inner environments. These single-crystal-to-single-crystal transformations are reversible evidenced by the structural studies of the dehydrated single crystals after exposure to humid air. Magnetic measurements showed antiferromagnetic coupling between the Cu^{2+} ions. Homometallic ferrimagnetism is observed below T_c of 2.4 and 3.4 K for the as-synthesized and the dehydrated samples, respectively.

Introduction

Open frameworks made of metal atoms or clusters of atoms interconnected by organic linkers have attracted significant interest mostly because of their potential for various applications such as gas storage, separation, catalysis, sensor technology, and so forth but also because of their many unique structural features.[1] Among them, frameworks with flexible but stable architectures may be capable of serving as hosts for various dynamic reversible processes upon external stimulations.[2−4] For example, some frameworks can intelligently adjust their porosities to fit the guest molecules by shrinking, expanding, and/or distorting. In the spectrum of rigidity, such frameworks are in the middle between the more typical rigid metal-coordination frameworks and the "soft" self-assembled materials based on supramolecular interactions.[5] One important advantage of such flexible structures is that they often maintain their crystallinity after modification and can be studied structurally. Knowledge of the modified structure can be then used to further tune various features such as magnetic properties, ion conductivity, chirality, and so forth, to eventually achieve multifunctional materials.[6] However, rational design of targeted frameworks is still very limited and even more so for flexible frameworks because manipulation of the flexibility of the framework is very difficult and barely explored.[2] It is believed that the presence of weak interactions is helpful for flexibility because such interactions can be modified with less energy input. Some empirical observations based on existing examples with single-crystal structural evidence indicate that upon external influence such frameworks adjust by (a) rotation of some parts of the organic ligands,[7,8] (b) sliding or moving of adjacent fragments,[9] (c) shrinking or expanding of soft ligands,[10] and (d) rearrangement of hydrogen bonds.[11] These actions are generally based on weak

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intermolecular interactions, and those involving strong chemical bonds are quite rare.[12,13]

Several of the limited number of flexible metal-containing frameworks are copper based.[8,14] The flexibility in these cases is associated primarily with changes of the coordination environment around the copper centers. This should not be surprising because copper has very versatile coordination chemistry and can readily adopt square-planar, square-pyramidal, trigonal bipyramidal, or octahedral coordination. Furthermore, the tendency for Jahn−Teller distortion of the d^9 Cu^{2+} ions provides additional capabilities for the frameworks to distort. All these indicate that Cu^{2+} is a good starting point for creating new flexible frameworks.

Removal of captured solvent molecules and its reversibility are perhaps the most often tested properties because the as-synthesized frameworks are typically not porous.[9−19] The removal is typically accomplished by heating the compounds in air, inert atmosphere, or under vacuum, and the crystallinity and identity of the resulting powders are established by powder X-ray diffraction. Single crystals of the as-synthesized compounds, however, tend to fragment into smaller pieces during the process. Thus, single-crystal-to-single-crystal studies are very rare[13,16−18] and are typically carried out on products where only noncoordinated molecules are removed.[17,18] Removal of coordinated ligands usually leads to macro-fragmentation although on the atomic scale the framework may retain overall structural integrity. Last, not much is known about the mechanism of the process and eventual intermediate stages between the starting and the final structures.

In an earlier communication we reported the reversible single-crystal-to-single-crystal dehydration (including coordinated water) under vacuum of two frameworks made of Co or Zn bridged by the nine-dentate linker tetrahydrofurane tetracarboxylate (THFTC).[16] In addition to the dehydration, the Zn compound displayed the unique phenomenon of reversible hopping of some of the zinc atoms during the de- and rehydration process. In light of these observations and the considerations discussed above, we extended our research onto Cu^{2+} system with the same THFTC ligand. We report here the synthesis and characterization of the compound $[Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)_2](H_2O)_4$ (**1**) as well as detailed structural studies of the mechanism of its reversible dehydration and rehydration.

Experimental Section

Synthesis. The starting materials, all of reagent grade, were used as received. Single crystals of **1** were obtained from hydrothermal reactions carried out in 23 mL Teflon lined autoclaves at 115 °C for 2 days. The autoclave was loaded with $CuCl_2 \cdot 2H_2O$ (227 mg, 1.33 mmol), H_4THFTC (55 mg, 0.22 mmol), NaOH (1.5 mL of 1 M solution, 1.5 mmol), and 3 mL of H_2O (final pH ∼ 5.0). After the reaction, the bomb was allowed to cool to room temperature slowly for 1 day. The product contained column-shaped greenish crystals (yield of ca. 60%) together with small amounts of fine powder. Higher temperature and longer reaction time were found to decrease the quality of the crystals and the yield of the reaction. An isostructural bromide can be synthesized following the same procedure while the iodide could not be isolated, most likely because of the redox reaction between Cu^{2+} and I^-.

Dehydration and Rehydration of 1. All experiments were carried out on single crystals of the compound. Different sets of crystals were enclosed in glass tubes and were kept under vacuum (mechanical pump) at room temperature for 1 week or at higher temperatures of 65, 105, 120, 135, and 160 °C for 1 day. It should be pointed out that none of the hydration and rehydration experiments as well as single-crystal X-ray data collections were carried out on one and the same crystal. The greenish crystals of the as-synthesized compound visibly start turning blue after a few hours even at room temperature. The process is much faster at higher temperatures, and the final color is different: blue for 65 °C, dark green for 105, 120, and 135 °C, and black for 160 °C. After cooling, the crystals were immediately covered with Paratone-N oil for protection from rehydration and were examined by single-crystal X-ray diffraction. The crystals heated at up to 135 °C remained single and transparent, and their structures were determined, while those heated at 160 °C became amorphous and opaque. The chemical formulas of the dehydrated samples derived from the structure determinations are $Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)_{2+x}$ with $x \approx 0.4$ for the room-temperature evacuation (**1-RT**), $Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)_2$ after heating at 65 °C (**1-65**), and $Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)$ after heating at 105 (**1-105**) and 135 °C (**1-135**).

For the rehydration process the dehydrated single crystals were exposed to ambient air at room temperature. At these conditions they turned back to the original greenish color in 2 days. Some of them were kept in a vial inserted in a covered beaker with some water. In this humid atmosphere their color changes back to the original color in less than 1 h.

Ammonia Uptake of 1-105. Some dark-green single crystals of **1-105** (dehydrated at 105 °C) were exposed to ammonia gas (by refilling the evacuated container with dry ammonia) at room temperature for 2 days. The color of the crystals changed to blue in a few hours but did not change to the original aqua-green of the as-synthesized compound **1**. They remained single, and the structure

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Table 1. Crystallographic Data for $[Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)_2](H_2O)_4$ (1) and Its Dehydrated, Rehydrated, and Ammonia-Exchanged Derivatives

compound	**1**	**1-RT**	**1-65**	**1-105**	**1-Re**	**1-NH3**
formula	$C_{16}H_{24}O_{28}Cl_2Cu_7$	$C_{16}H_{16.8}O_{24.4}Cl_2Cu_7$	$C_{16}H_{16}O_{24}Cl_2Cu_7$	$C_{16}H_{14}O_{23}Cl_2Cu_7$	$C_{16}H_{24}O_{28}Cl_2Cu_7$	$C_{16}H_{17}O_{23}NCl_2Cu_7$
M_r [g mol^{-1}]	1180.03	1115.2	1108.02	1089.95	1180.03	1107.03
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	Pc	Pc	Pc	$P2_1/c$	Pc
a [Å]	14.2604(2)	14.2291(2)	14.1851(2)	14.119(3)	14.2238(3)	14.1601(3)
b [Å]	10.1663(2)	10.0388(2)	10.0601(2)	10.043(2)	10.1417(2)	10.0452(2)
c [Å]	10.5637(2)	10.3413(2)	10.2537(2)	10.210(2)	10.5474(3)	10.2294(2)
β [deg]	91.8030(10)	92.4490(10)	92.2620(10)	92.16(3)	91.7950(10)	92.258(1)
V [Å^3]	1530.72(5)	1475.83(5)	1462.10(5)	1446.8(5)	1520.75(6)	1453.9(5)
Z	2	2	2	2	2	2
ρ_{calcd} [g cm^{-3}]	2.560	2.507	2.512	2.502	2.577	2.522
μ(Mo Kα) [mm^{-1}]	5.060	5.231	5.279	5.330	5.093	5.306
R1/wR2 ($I > 2\sigma(I)$)[a]	0.0252/0.0616	0.0335/0.0836	0.0257/0.0578	0.0230/0.0565	0.0228/0.0563	0.0288/0.0641
R1/wR2 (all data)[a]	0.0332/0.0638	0.0369/0.0907	0.0275/0.0584	0.0247/0.0574	0.0312/0.0586	0.0317/0.0649

[a] $R1 = [\sum||F_o| - |F_c||]/\sum|F_o|$; $wR2 = \{[\sum w[F_o^2 - F_c^2]^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = [\sigma^2F_o^2 + (AP)^2 + BP]^{-1}$ where $P = [F_o^2 + 2F_c^2]/3$.

was determined by single-crystal X-ray diffraction. The chemical formula derived from the structure determination of this derivative labeled **1-NH3** is $Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)(NH_3)$. When exposed to air the crystals of **1-NH3** change color toward green; however, they remained somewhat bluish and never reached the original light-green color.

Thermogravimetric Analysis (TGA). Thermogravimetric studies of compound **1** were carried out on a high-resolution Auto TGA 2950 analyzer both in air and in nitrogen gas (T_{max} = 600 °C, heating rate = 10 °C/s, plots in Supporting Information). The compound loses water both in air and in N_2 continuously from 65 °C up to 240 °C. The weight loss is 7.8% in both atmospheres, and this matches the calculated 7.6% for the loss of five water molecules that result in the overall stoichiometry $Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)$. In air, the sample decomposes to CuO (Cu_7O_7) in a single sharp step at approximately 250 °C with a loss of additional 44.4% of the initial weight (calcd 45.0%). In the N_2, the same sharp step at the same temperature accounts for a weight loss of only 20.3%. This is followed by a plateau to approximately 300 °C, at which temperature the sample loses another 21% of its weight and also forms CuO. Additional weight loss of 13% occurs continuously above approximately 400 °C and reaches a plateau at approximately 530 °C. This is associated with decomposition of CuO to Cu and O_2 (calcd 13.3%).

Structure Determinations. Data sets were collected on a Bruker APEX-II diffractometer with a CCD area detector at 100 K with Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL97 program.[20] More details of the data collections and structure refinements of **1**, **1-RT**, **1-65**, **1-105**, **1-Re** (a rehydrated crystal that was previously dehydrated at 105 °C), and **1-NH3** are presented in Table 1. The structure of **1-135** is exactly the same as that of **1-105** and is not listed in the table.

It should be pointed out that while the structures of **1**, **1-Re**, and **1-NH3** are refined in the centrosymmetric $P2_1/c$ space group, the structures of the dehydrated compounds **1-RT**, **1-65**, and **1-105** (and **1-135**) are acentric and were refined in the space group *Pc*. Apparently, the 2_1-axis and the inversion center associated with the combination of this axis and a *c*-glide are lost (confirmed by a PLATON check[21]) during the dehydration. (Numerous violations of the systematic extinction $0k0$, $k = 2n$, consistent with a 2_1 screw axis are listed in a table in Supporting Information.) This, as might be expected, leads to extensive racemic twinning and, indeed, all dehydrated structures were refined as racemic twins with almost equal fractions. The quality of the crystals does not change noticeably upon dehydration and rehydration. Specifically, the mosaicity does not change from crystal to crystal and stays within the range 0.6−0.7.

Magnetic Measurements. Measurements of the temperature dependence of the magnetic susceptibilities and the field dependence of the magnetizations of polycrystalline samples of **1** and **1-105** were performed on a Quantum Design MPMS SQUID system. The residual field for measurements at zero-field cooling was carefully adjusted to be below 0.1 Oe with the help of Gd_2O_3 as a reference sample. All experimental magnetic data were corrected for the diamagnetism of the sample holders and of the constituent atoms (Pascal's tables).

Results and Discussion

Crystal Structure of 1 and 1-Re. The crystal structures of the as-synthesized **1** and the rehydrated compound **1-Re** that was previously dehydrated at 105 °C (**1-105**) are exactly the same, and this confirms the complete reversibility of the dehydration process. The complex three-dimensional (3D) framework ($P2_1/c$) of the compound with stoichiometry $[Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)_2](H_2O)_4$ has five crystallographically unique copper sites, three of which, Cu1, Cu2, and Cu5, are at inversion centers while the other two are at general positions. There is also one fully deprotonated $THFTC^{4-}$ ligand, one Cl^- anion, two OH^- anions, and three water molecules in the asymmetric unit. The copper atoms are in different coordination environments (Figure 1a): Cu1 is in a slightly elongated octahedron (Cu1−O1 = 2.29 Å), Cu2 is square planar, Cu3 and Cu5 are in considerably elongated octahedra (Cu5−O2W = 2.44 Å, Cu3−Cl1 = 2.71 and 2.80 Å), and Cu4 is in an apically elongated square pyramid (Cu4−Cl1 = 2.75 Å). With the long Cu−O distances excluded, the remaining Cu−O bond lengths, 1.93−2.00 Å, are quite typical for Cu^{2+}. The Cu−Cl distances are relatively long and, together with the long Cu−O distances, attest to the Jahn−Teller distortions around Cu^{2+}.[22]

The deprotonated nine-dentate ligand $THFTC^{4-}$ coordinates to seven copper atoms via all of its nine oxygen atoms (Figure 1a). All four carboxylic groups act as bridges between pairs of metal centers. Two of them, O4−C6−O5,

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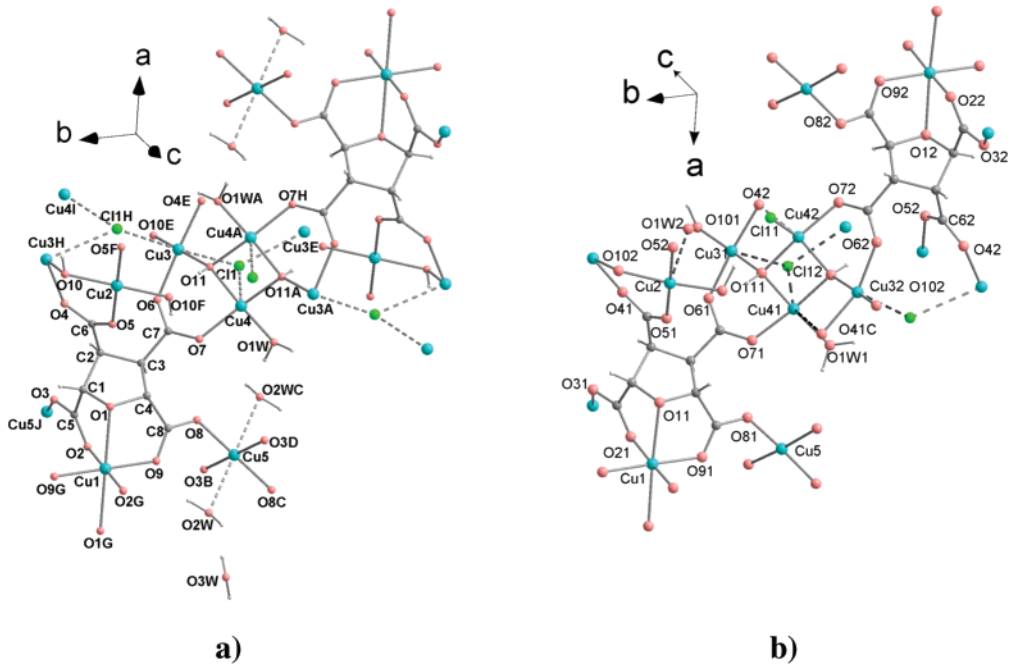

Figure 1. Local environments of the copper atoms and THFTC ligands in (a) **1** and (b) **1-65**. The broken lines represent weak interactions.

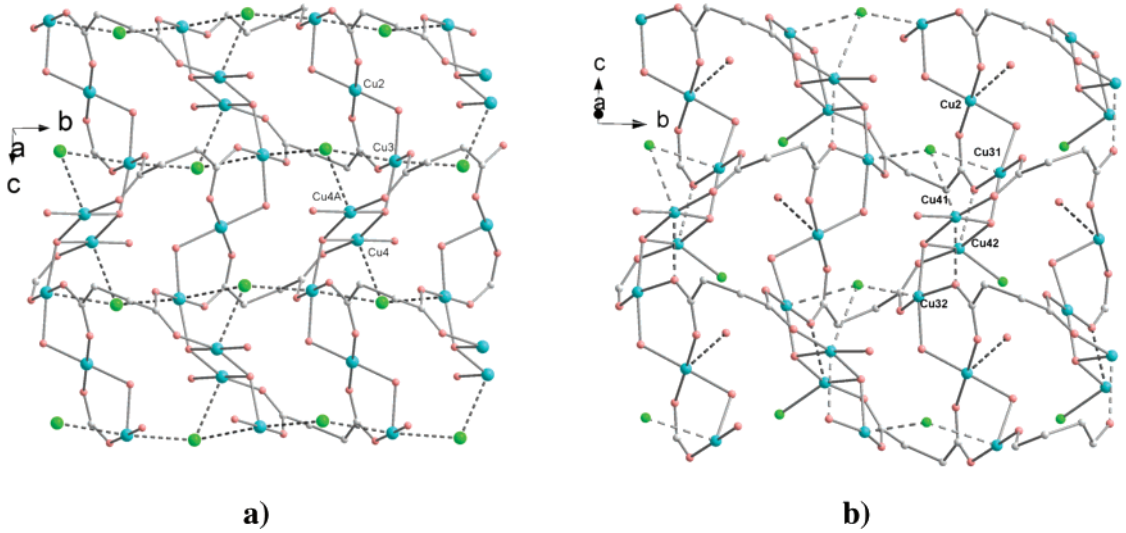

Figure 2. Shown is the repositioning of chlorine (green) and water molecules (terminal red atoms) within layer A upon dehydration of **1** (a) at 65 °C to produce **1-65** (b).

and O6−C7−O7, are in *syn*−*syn* mode and bridge within the pairs Cu2−Cu3 and Cu3−Cu4 while the other two, O2−C5−O3 and O8−C8−O9, are in *syn*−*anti* mode for two Cu1−Cu5 pairs. The weakly coordinated Cl^- anion is common for three metal centers, two of them Cu3 and one Cu4. The two hydroxyl groups in the structure also bridge between copper atoms, one in a μ_2-mode between Cu2 and Cu3 and the other in μ_3-mode between Cu3 and two Cu4 atoms. From a magnetic point of view, all these bridges keep the copper atoms at distances in the range 2.92−5.28 Å and can efficiently transmit magnetic coupling between them.[23]

The overall 3D structure of **1** can be viewed as a framework made of two types of layers, denoted as A and B, parallel to the *bc* plane and held together by THFTC linkers. Layer A contains three copper atoms, Cu2, Cu3, and Cu4, and all the Cl^- and OH^- anions (Figure 2a). Layer B is a (4,4) layer made of Cu1 and Cu5 that are held together by carboxylic groups and the oxygen atoms of the tetrahydrofurane rings of the THFTC ligands (Figure 3). The two layers alternate along *a*, and the THFTC linkers act as pillars (Figure 4). This creates galleries between the pillars which, in turn, form channels along the *c*-axis.

All coordinated and noncoordinated water molecules are in the channels of the framework and form hydrogen bonds between themselves (O1W−O2W = 2.74, O2W−O3W = 2.89, and O1W−O3W = 3.01 Å). For the purposes of the discussion concerning the dehydration and rehydration of the structure (below), it is important to describe in detail the local environments around the water molecules. Thus, O1W is very strongly coordinated to Cu4 at a distance of 1.97 Å, O2W is weakly coordinated to Cu5 at a distance of 2.44 Å, and O3W is a lattice water molecule that resides along the

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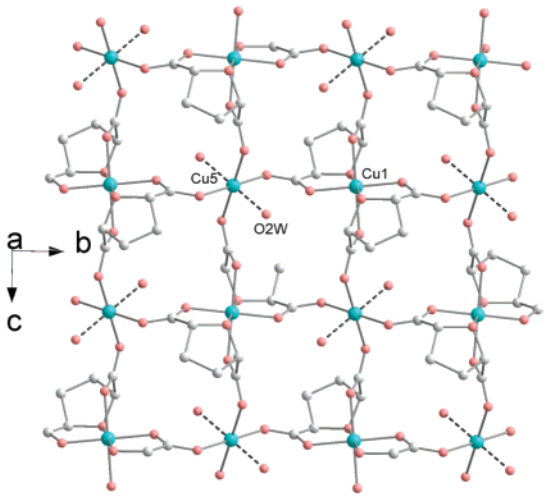

Figure 3. Layer B in the as-synthesized compound **1** (shown) does not change much upon dehydration. It only loses the weakly coordinated water O2W.

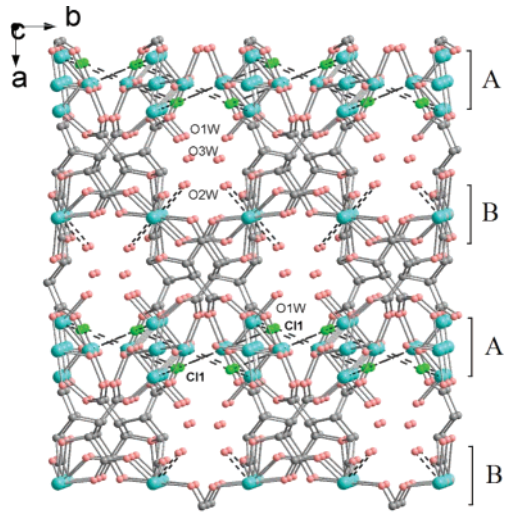

Figure 4. 3D framework of **1** with channels along *c* filled by water. It can be viewed as made of layers A and B parallel to *bc* (shown) and shown in Figures 2 and 3.

center of the channel and interacts with its surroundings only by hydrogen bonds. These three water molecules represent, therefore, three levels of bond strength, that is, strongly bonded, weakly bonded, and nonbonded. They provide an ideal opportunity for investigation of a stepwise dehydration process which, in this case, would start with the removal of O3W, proceed next with O2W, and finish with O1W. This will result in changes in the copper coordinations, but these changes may be absorbed by rearrangements in a flexible framework.

Crystal Structures of 1-RT and 1-65. When kept under vacuum at either room temperature or 65 °C the single crystals of the as-synthesized compound **1** change color from aqua green to blue. Structure determinations revealed that the structures of **1-RT** and **1-65** are nearly the same except for some small amount of water, that is, a stoichiometry $Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)_{2+x}$ with $x \approx 0.4$ for **1-RT** and $x = 0$ for **1-65**. At the same time the structure of the two compounds differs significantly from the original structure of **1**. Thus, the lattice water, represented by O3W in **1**, is completely removed while the weakly bonded water O2W is partially removed in **1-RT** (close to 80% removal) and completely removed in **1-65**. Furthermore, as a result of this water removal, half of the strongly coordinated water molecules O1W and Cl^- anions shift to new positions (Figure 1b).

As already mentioned, the two compounds crystallize in the acentric *P*c space group; that is, they lose the 2_1 screw axis and the inversion center of the $P2_1/c$ space group of the as-synthesized compound. This lowering in symmetry is driven by the different repositioning of formerly crystallographically equivalent atoms. The independent unit of **1-65** is twice that of **1** and has pseudo-inversion centers that relate most but not all atoms. The formerly equivalent strongly bonded O1W water molecules are now split to O1W1 and O1W2 that are completely unrelated (Figure 1b). Similarly, Cl1 in **1** becomes two unrelated atoms Cl11 and Cl12 (Figures 1b and 2b). These are the atoms that experience major relocation upon dehydration, and as a result of this, the coordination around some of the copper atoms changes significantly (visibly evident from the change of color). Thus, the coordination geometry around Cu2 changes from square planar to an apically elongated square pyramid with axial O1W2 at a distance of 2.55 Å. The octahedral Cu3 position in **1** loses one of the two chlorine ligands and the corresponding Cu31 and Cu32 atoms in **1-65** are also square pyramidal with four oxygen and one apical chlorine atom each (Figure 1b). One of the two positions derived from the square pyramidal Cu4 in **1**, Cu41, changes coordination environment to an elongated octahedron while the second one, Cu42, remains the same. Last, the elongated octahedron around Cu5 in **1** changes to a square-planar coordination after dehydration because the two weakly bonded O2W molecules are gone. The THFTC ligands remain nine-dentate, and the hydroxyl groups do not change substantially. The chlorine atoms, on the other hand, experience large shifts as half of them move much closer to Cu42 at 2.22 Å than to the parent Cu4 in **1** while the other half remain the same (Figures 1b and 2b). Although the dehydration process introduces some modifications to the structure, the overall framework does not change much and can be also viewed as made of layer A, but slightly modified (Figure 2b), and exactly the same layer B.

Crystal Structures of 1-105 and 1-135. The dehydrations at 105 and 135 °C produce dark green crystals with the same structure and stoichiometry $Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)$. The major difference between **1-65** and this structure is that one more water molecule per formula has been removed. These are the coordinated water molecules O1W2 in the former which are completely removed in the latter. Recall that the parent water molecule O1W in **1** is coordinated strongly to Cu4 at a distance of 1.97 Å, but its derivative O1W2 in **1-65** is very weakly coordinated to Cu2 at a very long distance of 2.55 Å. The weakened interactions when combined with the higher temperature apparently result in complete removal of this molecule. The final coordination environment of Cu2 changes back to square planar, and the color changes back to green.

Crystal Structure of 1-NH3. The overall structure of **1-NH3** is the same as that of **1-65** except for the guest

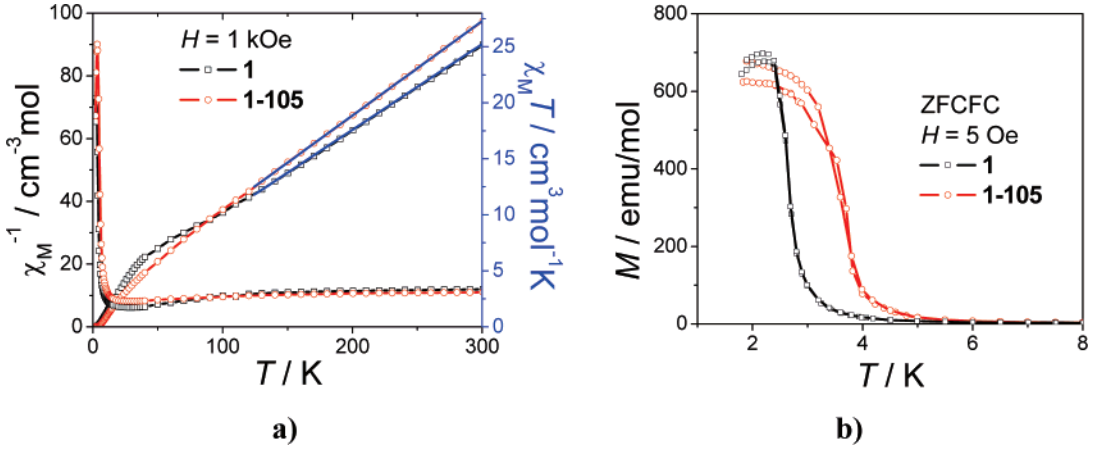

Figure 5. Plots of (a) the temperature dependence of χT and χ^{-1} for **1** and **1-105** and (b) the ZFC and FC curves for the same compounds at low temperatures and low field.

molecules coordinated to Cu2, NH_3 in the former and H_2O in the latter. However, because NH_3 and H_2O are indistinguishable by X-ray diffraction, our conclusions for the identity of the guest molecule are based on the experimental conditions (the dehydrated at 105 °C crystals were exposed to *dry* ammonia from a gas tank) and the color changes described above (the color of **1-NH3** is not the original light green of rehydrated crystals; it becomes that color after further exposure to moisture).

Magnetic Properties. The magnetic properties of **1** and **1-105** indicated that the dehydration affects slightly the magnetic critical temperatures but, overall, the magnetic properties remained quite similar. The χT values of 3.34 and 3.08 cm^3 K mol^{-1} at 300 K for **1** and **1-105** (calculated per formula unit with seven Cu atoms), respectively, decrease slightly with the temperature to shallow minima at about 28 K (Figure 5a). Below this temperature they increase abruptly, peaking at 2.5 and 3.5 K for **1** and **1-105**, respectively, and then drop again below these temperatures. The Curie−Weiss fits of the magnetic susceptibilities above 150 K provide Curie constants C of 3.61 and 3.32 cm^3 mol^{-1} K for **1** and **1-105**, respectively, while the Weiss temperatures are correspondingly −29.6 and −24.2 K. The Curie constants correspond to effective magnetic moments of 2.03 and 1.95 μ_B for **1** and **1-105**, respectively, and these values are well within the range observed for Cu^{2+}, 1.75−2.10[24a] and 1.7−2.2[24b] μ_B according to two different sources.[24] The corresponding g values of 2.34 and 2.25 for **1** and **1-105**, respectively, are somewhat high but very close to the upper limit of the reported range of typical values for Cu^{2+} in similar compounds, 2.0−2.3.[24b] The multiple magnetic pathways in the structures make the extraction of coupling parameters impossible. However, the negative Weiss constants clearly indicate dominant antiferromagnetic interactions between the Cu^{2+} ions for both samples.

The possibility for magnetic transitions suggested by the sharp peaks in the χT curves was further investigated by measuring the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations in the temperature range 1.8−15 K (Figure 5b). According to hysteresis measurements (see below) the two compounds are very soft magnets with almost zero coercive fields. Thus, the ZFC/FC measurements were carried out at a very low field of 5 Oe. The two curves are superimposed at higher temperatures for both compounds (Figure 5b). They increase abruptly at temperatures below 4 K and then diverge at around 2.4 and 3.4 K for **1** and **1-105**, respectively. This suggests the establishment of spontaneous magnetization arising from the onset of long-range ordering. The deviation points of the ZFC and FC curves define the critical temperatures of **1** and **1-105** as approximately 2.4 and 3.4 K, respectively (Figure 5b).

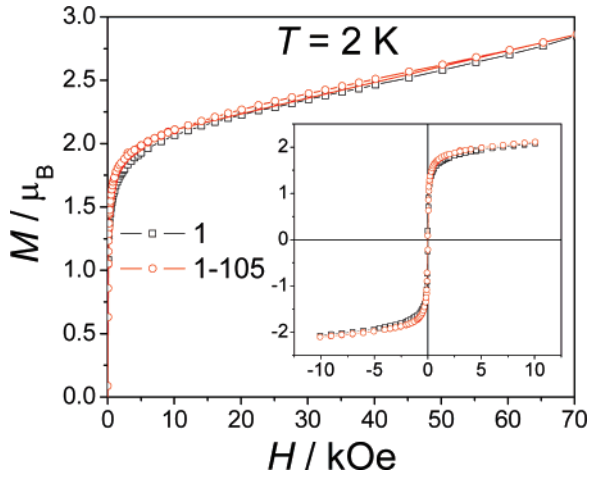

Figure 6. Plots of the field dependence of the magnetizations of **1** and **1-105** at 2 K in the field ranges 0 to 70 kOe and −10 to +10 kOe (inset).

The observed spontaneous magnetizations with mainly antiferromagnetic interactions are reminiscent of systems with ferrimagnetic ordering or weak ferromagnets with spin-canting.[23] To clarify the nature of the low-temperature magnetic ordering, we measured the isothermal field-dependent magnetizations $M(H)$ at 2 K at fields of up to 70 kOe (Figure 6). Neither of the two compounds showed hysteresis loops as can be seen from the plots of $M(H)$ at low fields of ±10 kOe (Figure 6, inset), and this is consistent with very soft magnets. The curves of the two compounds are exactly the same: they increase very quickly at very low field of below 1 kOe and then slow down above 5 kOe, and at 70 kOe they reach values of 2.85 and 2.86 μ_B for **1** and **1-105**, respectively, that are quite lower than the expected spin-only saturation for seven Cu^{2+} ions. The remnant

(24) (a) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203−283. (b) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986; pp 52−69.

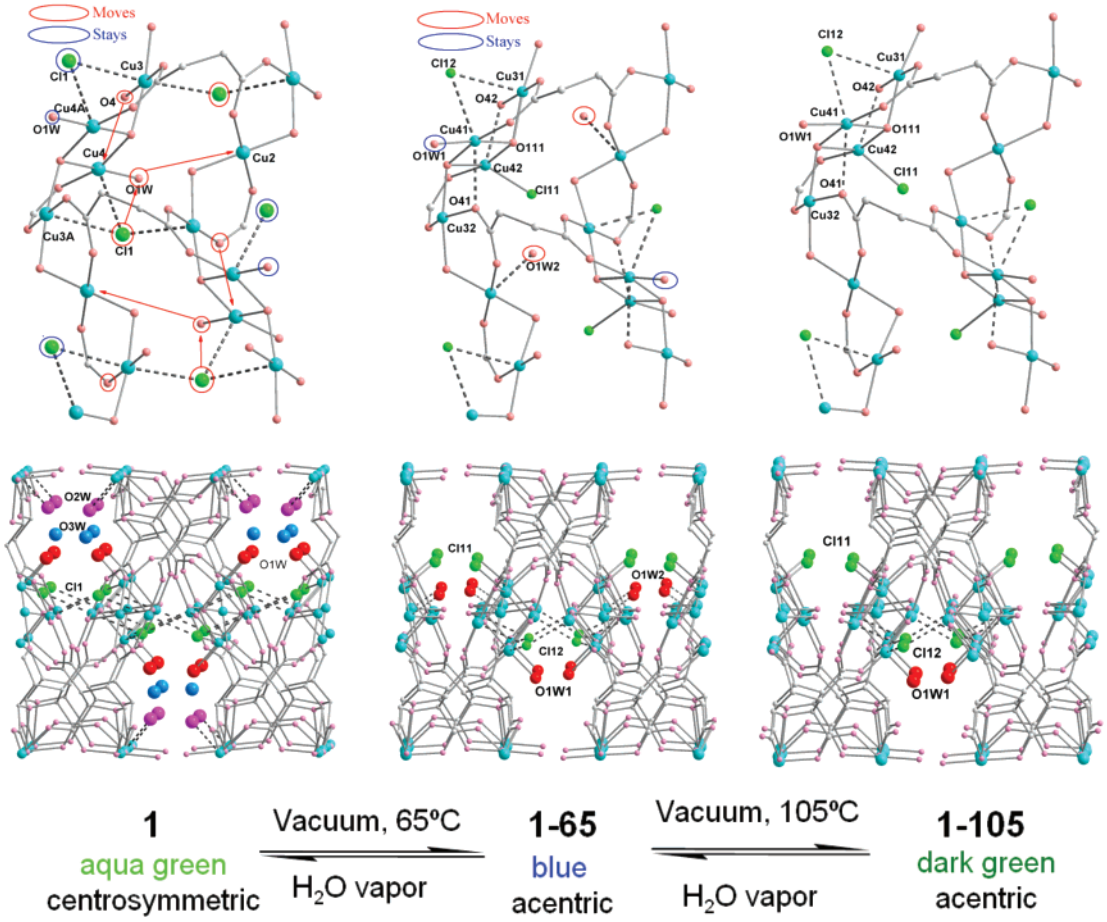

Figure 7. Dehydration process pictured in relocations that occur in layer A (upper row) and the corresponding view along the channels of the framework (lower row).

magnetization is too large for a spin-canted weak-ferromagnetic state and corresponds to an impossibly large canting angle of about 14°. It is rather consistent with a less common form of ferrimagnetism, namely, homometallic ferromagnetism, where equal spins are antiparallel but do not cancel overall. An imbalanced homospin system is difficult to achieve, and this makes rational design of homometallic ferrimagnets virtually impossible. Such materials are relatively rare and typically exhibit versatile magnetic coupling via azido or carboxylate bridges.[19,25]

Dehydration Process. The step-by-step dehydration process observed for **1** is a reversible process in a single-crystal-to-single-crystal transition in both directions. Furthermore, partial dehydration occurs even at room temperature under vacuum. The main "action" of the process, as already discussed, occurs in the A-type layers. Shown in Figure 7 are snapshots of this layer as well as of the 3D structure viewed along its channels as they change stepwise throughout the dehydration. The first step of the process is the loss of the lattice water O3W residing in the channels because it is only hydrogen-bonded to other water molecules and its removal is at a minimum energy cost. The weakly coordinated O2W, on the other hand, is more difficult to pull out, and its removal seems to be a continuous process that starts at room temperature under vacuum but cannot be completed without heating. The structure determination of **1-RT** clearly indicated some residual electron density at that position refined at about 40% occupancy. Upon removal of the noncoordinated and weakly coordinated water molecules, half of the strongly coordinated water O1W molecules become labile and move away from Cu4 to coordinate weakly to Cu2. Also repositioned are half of the chlorine atoms which move to fill the positions vacated by the repositioned O1W molecules and bond to Cu4. The major change in the framework itself is a small shift of one carboxylic oxygen atom, O4, which moves toward Cu4 and forms long Cu4−O4 bonds with distances of 2.39 and 2.50 Å in **1-65**. Of course, the exact sequence of these events is unknown, but a reasonable speculation is that the transfer of half of the strongly coordinated water O1W from Cu4 to Cu2 triggers the process. This removes the 2_1 screw axis, and the space group changes from centrosymmetric, $P2_1/c$, to acentric, *Pc*.

Increasing the temperature to 105 °C leads to further dehydration by removal of the water molecules weakly coordinated to Cu2 in **1-65**, that is, half of the original O1W molecules in **1** that moved from Cu4 to Cu2. At the same time, the other half of these O1W molecules, that is, those

(25) (a) Abu-Youssef, M. A. M.; Escuer, A.; Goher, M. A. S.; Mauter, F. A.; Rei*β*, G. J.; Vicente, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1624−1626. (b) Konar, S.; Mukherjee, P. S.; Zangrando, E.; Lloret, F.; Chaudhuri, N. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 1561−1653. (c) Gao, E. Q.; Yue, Y. F.; Bai, S. Q.; He, Z.; Yan, C. H. *J. Am. Chem. Soc.* **2004**, *126*, 1419−1429. (d) Li, J. T.; Tao, J.; Huang, R. B.; Zheng, L. S.; Yuen, T.; Lin, C. T.; Varughese, P.; Li, J. *Inorg. Chem.* **2005**, *44*, 4448. (e) Escuer, A.; Mautner, F. A.; Goher, M. A. S.; Abu-Youssef, M. A. M.; Vicente, R. *Chem. Commun.* **2005**, 605−607.

that remained coordinated to Cu4, remain in the structure and result in the stoichiometry $Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)$ for **1-105**. Our attempts to remove this sixth water molecule by raising the temperature to 135 °C were unsuccessful, and although the crystallinity of the compound remained intact, the water remained unchanged. Unfortunately, further temperature increase to 160 °C destroys the crystallinity, and the result is an amorphous phase. The TGA results confirm that only five water molecules can be removed from the compound without framework collapse. However, at ambient pressure the latter process occur at a substantially higher temperature of 250 °C. Apparently, the sixth water molecule is needed for completing the coordination around some of the copper atoms, and when removed, the whole structure collapses because of its inability to undergo any further distortions that may lead to reasonable copper coordination.

Conclusions

The mechanism of dehydration of the open-framework compound $[Cu_7Cl_2(THFTC)_2(OH)_4(H_2O)_2](H_2O)_4$ involves sequential removal of three different types of water molecules. As it might be expected, the most labile water leaves first while some of the most strongly coordinated water molecules do not leave at all. The step-by-step process starts at temperatures as low as room temperature under vacuum and is completed at 105 °C. The reversed process of hydration with complete restoration of the original structure occurs also at room temperature. During such a cycle the space group of the structures changes from centrosymmetric $P2_1/c$ to acentric Pc and back to $P2_1/c$. This overall flexibility is possible because of the capability of copper to readily change coordination environments. Both hydrated and dehydrated compounds are homometallic ferrimagnets. Studies of the ability of the dehydrated samples to absorb other guest molecules are in progress.

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Supporting Information Available: X-ray crystallographic CIF files for all compounds in this work, the TGA curves of **1** in N_2 and in air, and a table of the observed violations of the systematic condition for a 2_1 axis in the structures refined in space group *Pc* (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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