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Communication

Dramatic Solid-State Humidity-Induced Modification of the Magnetic Coupling in a Dimeric Fluorous Copper(II)−Carboxylate Complex

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The very fast and efficient water vapor absorption of the dimeric fluorous copper(II)−carboxylate complex $[Cu_2(C_8F_{17}CO_2)_4(acetone)_2]$ (**1**) leads, in the solid state, to a dramatic decrease of the exchange magnetic coupling between the copper(II) ions and to a drastic change of its powder EPR spectrum.

Crystalline materials exhibiting guest-modulated magnetic properties are of special interest for potential application in sensing.[1] As far as water detection is concerned, the materials described so far are based on porous or nanoporous purely inorganic or mixed inorganic/organic coordination polymers exhibiting long-range magnetic ordering.[2] We wish now to report on a different strategy based on the nonporous 0D crystalline fluorous dicopper(II)−carboxylate complex **1**. We found that **1**, in the solid state, exhibits a high affinity for water vapor and that, upon hydration, a fast and quantitative structural transformation occurs, leading to a dramatic decrease of the exchange magnetic coupling between the copper(II) ions.

The dimeric complex $[Cu_2(C_8F_{17}CO_2)_4(acetone)_2]$ (**1**) was prepared in 85% yield by reacting 2 equiv of the triethylammonium salt of the perfluorinated carboxylic acid with Cu(OTf)$_2$ in acetone.[3] Large blue-green parallelepipedic crystals of **1** were grown by allowing an acetone solution to stand at 4 °C for several days.

Single-crystal analysis revealed that **1** displays the classical "paddle-wheel" structure in which the two copper(II) ions are bridged by four carboxylates in a syn−syn configuration ($d_{Cu\cdots Cu}$ 2.737 Å), while two acetone molecules occupy axial coordination sites (Figure 1).[4] Importantly, no water molecules are present in the crystal lattice. For two of the four perfluorooctyl chains, the $C_\gamma−C_\delta$ bond adopts a gauche conformation, while all of the other C−C bonds display the anti geometry. Such isomerization, previously observed in various crystal structures of fluorous transition metal complexes,[5] is most probably induced by crystal packing effects and leads to both intra- and intermolecular interactions between the fluoroalkyl chains (Figure 1). Interestingly, the average Cu−O$_{carb}$ bond length of 1.974 Å is significantly higher than those observed in copper(II)−carboxylate dimers, which are typically in the range 1.960−1.970 Å.[6] This

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(3) See the Supporting Information for full details. Because of the high sensitivity of **1** towards humidity, crystals or powdered crystals of **1** should be stored under an inert atmosphere (glovebox, or sealed tube).

(4) Crystal data for $[Cu_2(C_8F_{17}CO_2)_4(acetone)_2]$, **1**: $C_{42}H_{12}Cu_2O_{10}F_{68}$, $M_r = 2095.52$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9.9252(1)$, $b = 11.9339(2)$, $c = 14.6689(2)$ Å, $\alpha = 71.087(1)$, $\beta = 83.369(1)$, $\gamma = 81.262(1)°$, $V = 1620.52(4)$ Å^3, $\rho_{calcd} = 2.147$ g cm^{-3}, $T = 125$ K, μ(Mo Kα) = 0.71073 Å, 9769 unique reflections, 6870 observed ($I > 2\sigma I$), $R_{int} = 0.0172$, $\theta_{max} = 31.61°$, final $wR_2 = 0.227$ (all data), $R_1 = 0.073$.

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(6) See, for example: (a) Stephens, J. C.; Khan, M. A.; Houser, R. P. *Inorg. Chem.* **2001**, *40*, 5064. (b) Lah, N.; Giester, G.; Lah, J.; Šegedin, P.; Leban, I. *New J. Chem.* **2001**, *25*, 753. (c) Huang, H.; Yu, S.-H.; Liu, H.-B.; Shi, M. *Polyhedron* **2004**, *23*, 55.
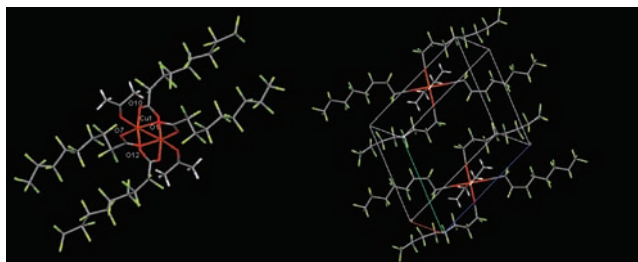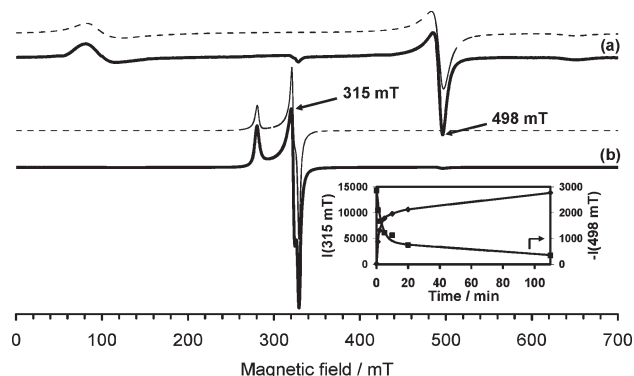
Figure 1. Molecular structure of $[Cu_2(C_8F_{17}COO)_4(acetone)_2]$ (**1**) and a view of the crystal lattice along the Cu−Cu axis. Cu, orange; C, gray; O, red; F, green; H, white. Selected bond distances (Å): Cu1−O1, 1.986(4); Cu1−O7, 1.964(4); Cu1−O10, 1.968(4); Cu1−O12, 1.976(4).
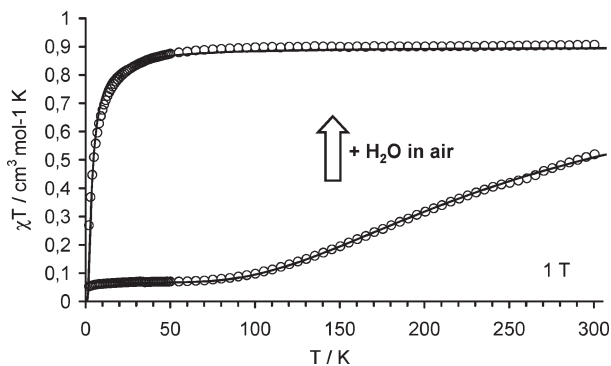
Figure 2. Experimental (○) and calculated (−) magnetic susceptibilities plotted as χT versus T of crystals of **1** (lower curve) and hydrated **1** obtained from powdered crystals of **1** exposed to the air for 24 h.

most likely reflects weaker Cu−O_{carb} bonds in **1** compared to other dimers, which could be attributed to a reduced electron density on the oxygen atoms due to the strong electron-withdrawing effect of the perfluoroalkyl chains. The weakening of the Cu−O bonds in **1** might contribute to the properties described below by facilitating the rearrangement of the coordination sphere occurring during the hydration process.

The magnetic susceptibility of **1**, χ, has been measured from 300 to 2 K under a field strength of 1 T (Figure 2). At 300 K, the value of χT is 0.51 cm^3 mol^{-1} K, which is far from the theoretical value of 0.75 cm^3 mol^{-1} K (for 2 Cu^{2+} ions d^9, $S = 1/2$ with $g = 2$). Upon cooling, the χT product continuously decreases to reach a minimum value at 0.06 cm^3 K mol^{-1} below 50 K. This behavior is consistent with a large antiferromagnetic coupling between the copper ions, leading to an $S = 0$ ground state and an $S = 1$ excited state. These magnetic data have been modeled with one spin dimer composed of two $S = 1/2$ Cu^{2+} ions. In this case, the Bleaney−Browers model[7] gives an analytical expression of χT (Supporting Information). The best set of parameter values using this model is $2J = -480$ cm^{-1} and $g = 2.3$, which is typical of "paddle-wheel" copper(II)−carboxylate complexes.[8] The powder X-band EPR spectrum of **1** (Figure 3)

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Figure 3. (a) Room-temperature X-band powder EPR spectra of **1** (simulated spectra in dashed line) and after exposure of the powder to air for 110 min (b). The inset shows the kinetics of the appearance of hydrated **1** and disappearance of **1** (see Figure S6 and experimental details provided in the Supporting Information).

recorded at room temperature (EPR tube prepared in a glovebox and sealed to avoid water uptake) is typical of a Cu(II)−carboxylate dimer with strong antiferromagnetic coupling between the copper ions,[9] the signal arising from the $S = 1$ excited state ($g_{x,y} = 2.057$, $g_z = 2.372$, $|D| = 0.405$ cm^{-1}, $E/D = 0$).[10]

Interestingly, when a powdered sample of **1** (5 mg) is exposed to air (relative humidity = 60%), the signal arising from **1** disappears rapidly while, at the same time, an intense rhombic signal of an $S = 1/2$ species ($g_x = 2.41$, $g_y = 2.096$, $g_z = 2.052$) attributed to magnetically isolated Cu(II) ions appears (Figure 3). The transformation is fast since about 65% of the solid is transformed within 5 min and highly efficient, as the signal of **1** completely disappears within 4 h. An excellent correlation was observed between the kinetics of disappearance of **1** and the appearance of hydrated **1** (inset of Figure 3).

Magnetic measurements performed on the hydrated powder of **1** confirm the quantitative transformation of **1** into a structure in which the copper(II) ions behave as magnetically isolated ions at room temperature (Figure 2).

The value of the χT product exhibits a plateau from 300 to 50 K having a value of 0.9 cm^3 K mol^{-1}, decreasing to a value of 0.27 cm^3 K mol^{-1} at 2 K and revealing a small but nonzero antiferromagnetic coupling between the metal ions. In agreement with EPR and IR data, we used the same dimer model as for compound **1**. A satisfactory fit of the susceptibility data with the Bleaney−Browers equation was obtained with $2J = -7$ cm^{-1} and $g_{iso} = 2.2$, using $[Cu_2(C_8F_{17}CO_2)_4(H_2O)_6]$ as the chemical formula for hydrated **1** in accordance with weight variation measurements performed during the hydration process (Figure S1, Supporting Information) and thermogravimetric analysis (Figure S3, Supporting Information). On the TG diagram, a weight loss ranging from 5 to 6% is observed between 70 and 200 °C corresponding to the release of six to seven water molecules (calcd, 5.2% for 6 H$_2$O). It also shows that decarboxylation begins around 250 °C.
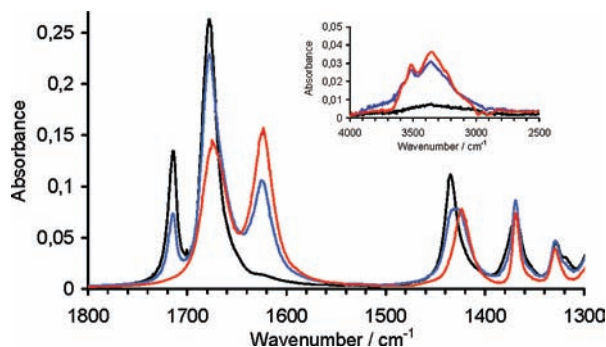
The drastic change in the magnetic interaction suggests a modification of the coordination mode of the carboxylates in hydrated **1**. Attenuated total reflectance− Fourier transform infrared (ATR-FTIR) spectroscopy provided insights into the chemical transformations occurring in the solid upon

(10) The parameters have been confirmed by simulation of the Q-band EPR spectra recorded at room temperature (Supporting Information).

Figure 4. ATR-FTIR spectra of **1** (black), after exposure in air for 3 min (blue), and 45 min (red) corresponding to the fully hydrated **1**. The inset shows the O–H stretching vibrations region.

hydration of **1** (Figure 4).[11] Exposing freshly powdered crystals of **1** to the air for a few minutes leads to the fast uptake of water molecules (inset of Figure 4), as shown by the appearance of a broad band from 3000 to 3650 cm^{-1} corresponding to O–H stretching vibrations. Additionally, the sharper peak at 3512 cm^{-1} is characteristic of the O–H frequency of coordinated water molecules. Simultaneously with the water uptake, the acetone ligands are released from the solid, as shown by the complete disappearance of their corresponding C=O stretching vibrations at 1714 cm^{-1}. At the same time, the asymmetric C=O stretching vibrations of the bridging carboxylate at 1678 cm^{-1} are decreasing while a new C=O band appears at 1623 cm^{-1}, affording two C=O bands of the same intensity for hydrated **1**.
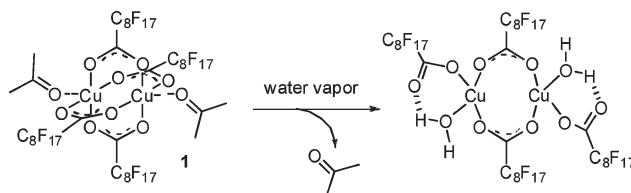
To account for these changes in magnetic and spectroscopic properties upon exposure to the air, we propose that the coordination of water molecules would partially displace the bridging carboxylates to afford a structure possessing both bridging and unidentate carboxylates (Scheme 1). The new C=O vibration at a lower frequency suggests a unidentate carboxylate strongly H-bonded to coordinated water molecules, as observed when the copper(II) acetate dimer is dissolved in water.[12] It is also well-established that intramolecular hydrogen bonds stabilize the unidentate coordination mode of carboxylates ligands in copper(II) complexes.[6a,6b,13]

Scheme 1. Proposed Structural Rearrangement Involving the Carboxylate Ligands to Account for the Observed Changes of the Magnetic Properties[a]

[a] Only the water molecules that are expected to induce a carboxylate shift are represented.

Additionally, hydrated **1** exhibits similar spectroscopic (IR, EPR) and magnetic properties to those of the structurally characterized copper(II)–carboxylate dimer [Cu$_2$(C$_6$H$_3$-Cl$_2$OCH$_2$COO)$_4$(bipyam)$_2$] possessing two bridging and two unidentate carboxylates.[14] Finally, the structural transformations occurring upon hydration of **1** might be reminiscent of what was described recently during the reversible sorption/desorption of gaseous EtOH in a single-crystal-to-single-crystal transformation within a silver(I)–fluorous carboxylate coordination polymer.[15]

In conclusion, we have reported the first example of a solid-state transformation of a copper(II)–carboxylate dimer induced by the absorption of water vapor. The fast and highly efficient water uptake in the solid state leads to both a dramatic decrease of the exchange magnetic interaction within the dimer and to a drastic change of its spectroscopic properties.

Supporting Information Available: Synthesis, additional IR, thermogravimetric, EPR, magnetic and crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

(11) Single-crystal X-ray diffraction analysis performed on crystals of **1** exposed to the air for several days revealed that the hydrated crystals of **1** become amorphous. The X-ray powder pattern of hydrated **1** is given in the Supporting Information (Figure S7).
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