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Crossover between Three-Dimensional Antiferromagnetic and Ferromagnetic States in Co(II)Cu(II) Ferrimagnetic Chain Compounds. A New Molecular-Based Magnet with $T_c = 38$ K and a Coercive Field of 5.66×10^3 Oe

Scott Turner,[†] Olivier Kahn,*[,†] and Louis Rabardel

Contribution from the Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS No. 9048, 33608 Pessac, France

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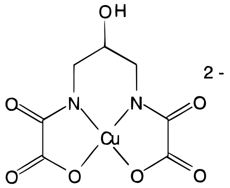
Abstract: $CoCu(pbaOH)(H_2O)_3{\cdot}2H_2O$ (**1**) is a Co(II)Cu(II) chain compound in which the ferrimagnetic chains interact antiferromagnetically within the lattice. Removing the two noncoordinated water molecules through a thermal treatment results in the new chain compound $CoCu(pbaOH)(H_2O)_3$ (**2**) which exhibits a ferromagnetic ordering of the ferrimagnetic chains at $T_c = 9.5$ K. Removing a third water molecule, occupying the apical position in the copper coordination sphere, results in $CoCu(pbaOH)(H_2O)_2$ (**3**) which again exhibits a three-dimensional ferromagnetic ordering, but at $T_c = 38$ K. The field dependence of the magnetization for **3** reveals a coercive field of 5.66×10^3 Oe at 2 K, probably a record in the field of molecular-based magnets. This dehydration process giving rise to a crossover between long-range antiferro- and ferromagnetic states is reversible, and can be repeated.

Introduction

The first molecular-based magnets were described a decade ago,[1−4] and in the last few years a number of new compounds of this type have been reported.[5−10] In many cases, these compounds contain two kinds of spin carriers, either two different metal ions,[11−16] or a metal ion and an organic radical.[17−24] In at least two cases, three spin carriers are involved.[25−27]

Our specific strategy to design molecular-based compounds exhibiting a spontaneous magnetization below a critical temperature T_c consists in assembling ferrimagnetic chains or layers within the crystal lattice in a ferromagnetic fashion. Along this line, we extensively investigated the $[Cu(pbaOH)]^{2-}$/Mn(II) system, where $[Cu(pbaOH)]^{2-}$ is the Cu(II) precursor:



with pbaOH standing for 2-hydroxy-1,3-propylenebis(oxamato).[4,28,29] Three compounds have already been characterized, namely $MnCu(pbaOH)(H_2O)_3{\cdot}2H_2O$ (**4**), $MnCu(pbaOH)(H_2O)_3$ (**5**), and $MnCu(pbaOH)(H_2O)_2$ (**6**). The crystal structures of **4** and **5** have been solved; both consist of oxamato-bridged Mn(II)Cu(II) chains.[4,28] In **4**, the chains run along the *a*-axis direction of the monoclinic lattice, and the shortest interchain metal−metal separations along the *b*- and *c*-axis directions are of the type Mn−Mn and Cu−Cu. Moreover, two non-

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[†] Laboratoire des Sciences Moléculaires.

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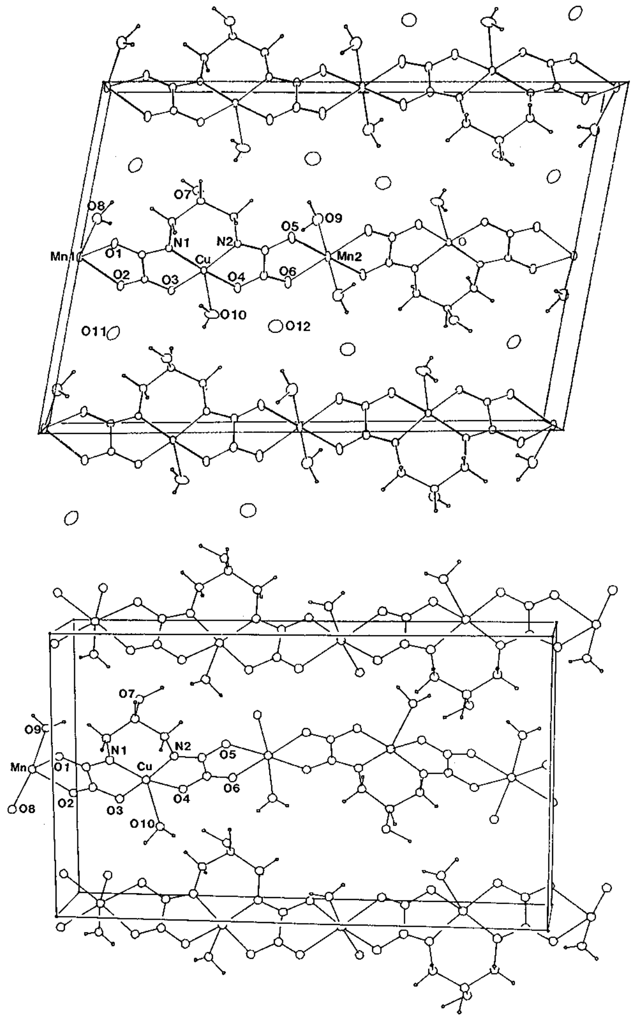

Figure 1. Perspective views of three neighboring chains in MnCu(pbaOH)$(H_2O)_3\cdot 2H_2O$ (**4**) (top) and MnCu(pbaOH)$(H_2O)_3$ (**5**) (bottom) (reprinted with permission from ref 28).

coordinated water molecules are hydrogen bonded to the chains. These water molecules can be easily removed, which affords compound **5**. Along one of the crystallographic directions perpendicular to the chain axis for **5**, the shortest interchain metal−metal separations are of the type Mn−Cu. Figure 1 emphasizes the structural differences between **4** and **5**. The crystal structure of **6** is not known; however, optical studies reveal that the additional water molecule which is removed with respect to **5** occupied the apical position in the copper coordination sphere.[29] Let us now recall briefly the magnetic properties of compounds **4**−**6**. All three present a minimum in the $\chi_M T$ versus T curves, χ_M being the molar magnetic susceptibility and T the temperature, which is characteristic of a ferrimagnetic behavior. **4** is a metamagnet with a three-dimensional antiferromagnetic ordering in zero field at 2.3 K, and a ferromagnetic-like transition within a critical field of 0.9×10^3 Oe. Compound **5** exhibits a three-dimensional ferromagnetic ordering of the ferrimagnetic chains at $T_c = 4.6$ K. Finally, **6** also shows a long-range ferromagnetic ordering, but at higher temperature; T_c is then equal to 30 K. Both **5** and **6**, below T_c, may be considered as soft magnets; the coercive field is of the order of 50 Oe.

A magnet is characterized not only by its critical temperature, but also by its coercivity and remnant magnetization. It is the coercivity which confers a memory effect on the ferri- or ferromagnetic materials. Recently, we discovered that replacing the magnetically isotropic Mn(II) ion by the strongly anisotropic Co(II) ion in related compounds results in a dramatic increase of the coercivity along with a significant increase of the critical temperature.[27] It was then worth investigating the $[Cu(pbaOH)]^{2-}$/Co(II) system. This paper will be devoted to this investigation. We will compare the magnetic properties of three Co(II)Cu(II) compounds, namely [CoCu(pbaOH)$(H_2O)_3\cdot 2H_2O$ (**1**), [CoCu(pbaOH)$(H_2O)_3$ (**2**), and CoCu(pbaOH)$(H_2O)_2$ (**3**). The first of these three compounds has already been described.[30] It is strictly isomorphous with compound **4**.

Experimental Section

Syntheses. CoCu(pbaOH)$(H_2O)_3\cdot 2H_2O$ (**1**) was synthesized by a method slightly different from that previously described.[30] Na_2[Cu(pbaOH)]$\cdot 3H_2O^4$ (552 mg, 1.4×10^{-3} mol) was dissolved in the minimum amount of water, giving a clear purple solution. $Co(NO_3)_2\cdot 6H_2O$ (408 mg, 1.4×10^{-3} mol) was also dissolved in the minimum amount of water. The two solutions were mixed and stirred at ambient temperature. After 10 min, a deep blue precipitate formed, and the mixture was stirred for a further 30 min to ensure completion. The blue solid was isolated by filtration, washed with water, and dried under vacuum at ambient temperature, then allowed to stand in air, affording a bright blue powder. Anal. Calcd for $C_7H_{16}N_2O_{12}CoCu$ (**1**): C, 18.99; H, 3.64; N, 6.33; Co, 13.31; Cu, 14.35. Found: C, 18.68; H, 3.76; N, 6.21; Co, 13.18; Cu, 14.21.

CoCu(pbaOH)$(H_2O)_3$ (**2**) was prepared by heating **1** gradually from ambient temperature to 102 °C under an atmosphere of dry N_2 over 2.5 h. Anal. Calcd for $C_7H_{12}N_2O_{10}CoCu$ (**2**): C, 20.68; H, 2.97; N, 6.89; Co, 14.49; Cu, 15.63. Found: C, 20.71; H, 2.64; N, 6.76; Co, 14.29; Cu, 15.49.

CoCu(pbaOH)$(H_2O)_2$ (**3**) was prepared by heating **1** at 120 °C under vacuum for 3 h. There is a gradual change of color from blue to deep purple. This purple color persists for several minutes when the sample is exposed to air, whence it reverts to the initial bright blue color. Anal. Calcd for $C_7H_{10}N_2O_9CoCu$ (**3**): C, 21.63; H, 2.59; N, 7.21; Co, 15.16; Cu, 16.35. Found: C, 21.52; H, 2.45; N, 7.40; Co, 15.25; Cu, 16.54.

Thermogravimetric Measurements. These were carried out with a Setaram TAGDSC apparatus, in the range 24−120 °C under an atmosphere of N_2.

Magnetic Measurements. These were performed with a Quantum Design MPMS-5S SQUID magnetometer, working both in the dc and ac modes. All the dc susceptibility versus temperature curves were recorded using a magnetic field of 10^2 Oe. All the ac susceptibility measurements were recorded at a field alternation frequency of 125 Hz and a drive amplitude of 1 Oe. It was checked that the ac response was not frequency-dependent. Magnetization versus field studies were performed in the field range $\pm 5 \times 10^4$ Oe.

Thermogravimetric Analysis

Figure 2 shows the overlays of time versus temperature and versus percentage change in weight for a sample of compound **1**. Initially, the temperature was increased at 30 °C per hour, giving a region of rapid weight loss between 24 (inflexion point T_1) and 102.1 °C (inflexion point T_2). The percentage weight loss at T_2 corresponds to 2.2 mol of water per CoCu unit. T_2 is the temperature where compound **2** was prepared. After this point, there is a more gradual loss of weight between T_2 and T_3. T_3, equal to 112.3 °C, occurs after the maximum temperature of 120 °C has been passed, and the sample has begun to cool down at 60 °C per hour. At T_3, the sample has lost 3.0 mol of water per CoCu unit. Once the sample has reached equilibrium during the cooling cycle, it begins to slowly reabsorb water.

Magnetic Properties. (a) CoCu(pbaOH)$(H_2O)_3\cdot 2H_2O$ (1). The temperature dependence of the magnetic susceptibility for this compound has already been reported. For completeness,

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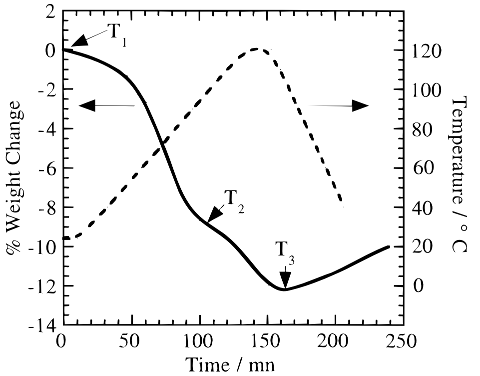

Figure 2. Overlay of temperature and percentage weight loss versus time, obtained by a thermogravimetric study of $CoCu(pbaOH)(H_2O)_3 \cdot 2H_2O$ (**1**).

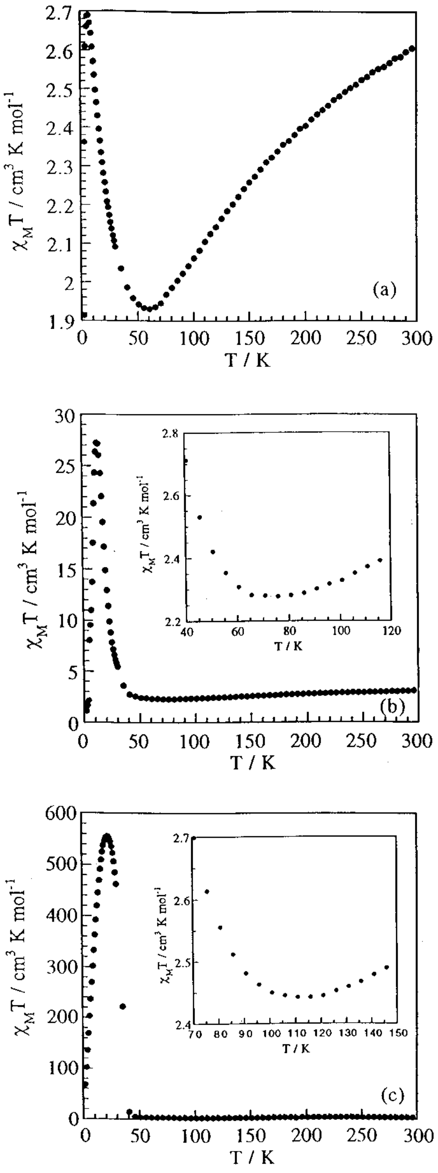

Figure 3. $\chi_M T$ versus T plots for compounds **1** (a), **2** (b), and **3** (c). The inserts emphasize the minima in the $\chi_M T$ versus T curves, characterizing a ferrimagnetic behavior.

the $\chi_M T$ versus T curve is recalled in Figure 3a. $\chi_M T$ is equal to 2.60 cm^3 K mol^{-1} at 290 K, decreases down to 1.91 cm^3 K mol^{-1} as the temperature is lowered down to 60 K, then increases at T is lowered further. $\chi_M T$ presents a maximum of 2.69 cm^3 K mol^{-1} at 7 K. Let us qualitatively discuss these magnetic susceptibility data. In the absence of magnetic interaction, $\chi_M T$ would be equal to $(\chi_M T)_{Co} + (\chi_M T)_{Cu}$, i.e. to the sum of what is expected for octahedral Co(II) and square-pyramidal Cu(II) ions. $(\chi_M T)_{Co}$ at 300 K is about 2.5 cm^3 K mol^{-1}; this value takes into account an important orbital contribution in addition to the $S_{Co} = {}^3/_2$ local spin.[6] $(\chi_M T)_{Cu}$ at 300 K is about 0.4 cm^3 K mol^{-1}. One sees that the observed $\chi_M T$ value at room temperature is already lower than $(\chi_M T)_{Co} + (\chi_M T)_{Cu}$, which reveals a rather large Co(II)−Cu(II) antiferromagnetic interaction. The decrease of $\chi_M T$ at T is lowered down to 60 K corresponds to a short-range order where the local angular momenta for Co(II) and Cu(II) are aligned antiparallel but have no correlation with neighboring CoCu units. As T is lowered further, below 60 K, the randomizing thermal effects are reduced and the correlation length increases. The maximum of $\chi_M T$ at 7 K reveals antiferromagnetic correlations between the ferrimagnetic chains. On the other hand, χ_M continuously increases as T is lowered down to 2 K, which means that the three-dimensional antiferromagnetic ordering should occur below 2 K.

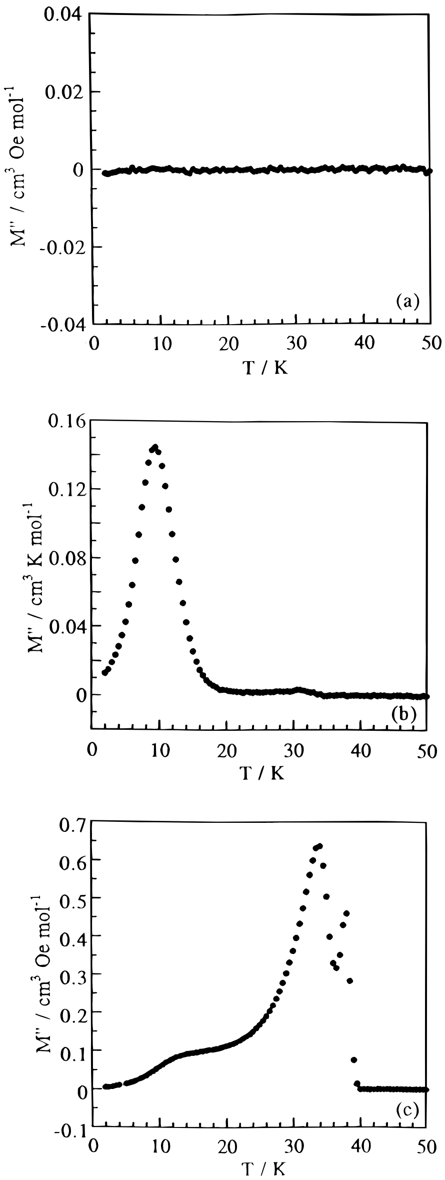

Figure 4. Out-of-phase component of the ac susceptibility versus T plots for compounds **1** (a), **2** (b), and **3** (c).

As expected, the out-of-phase component of the ac susceptibility is a straight line of zero magnetization (Figure 4a). For

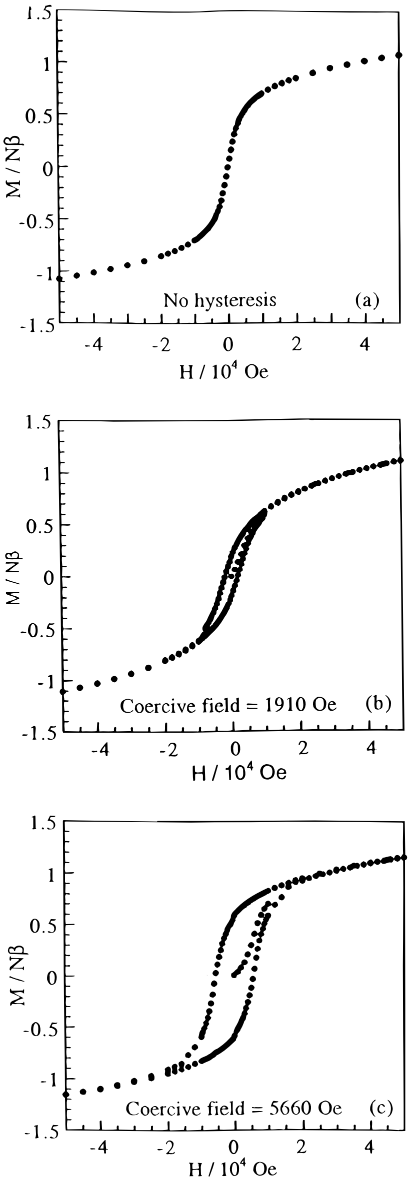

Figure 5. Cycled field dependence of the magnetization at 2 K for compounds **1** (a), **2** (b), and **3** (c).

comparison purposes the cycled magnetization versus field curve, which evidently presents no hysteresis, is represented in Figure 5a.

(b) CoCu(pbaOH)(H_2O)$_3$ (2). The $\chi_M T$ versus T curve for **2** is represented in Figure 3b. $\chi_M T$ is equal to 3.04 cm^3 K mol^{-1} at 300 K, shows a minimum at 70 K with $\chi_M T = 2.25$ cm^3 K mol^{-1}, then shows a sharp maximum at 9.5 K with $\chi_M T = 27.2$ cm^3 K mol^{-1}, corresponding to a three-dimensional ferromagnetic ordering. As a matter of fact, the out-of-phase component of the ac susceptibility shows a peak at $T_c = 9.5$ K (Figure 4b).

The field dependence of the magnetization of 2 K reveals a coercive field equal to 1.91 × 10^3 Oe (see Figure 5b). The magnetization at 50 kOe is equal to 1.1 Nβ, while the saturation magnetization is expected to be of the order of ($g_{Co}S_{Co} + g_{Cu}S_{Cu}$) = 2 N$\beta$, g_{Co} and g_{Cu} standing for the local Zeeman factors, and S_{Co} and S_{Cu} for local spins, respectively. This saturation magnetization corresponds to the situation where all the S_{Co} local spins (including the orbital contribution) are aligned along the field direction and all the S_{Cu} local spins along the opposite direction. In fact, the magnetization measurements were performed on powder samples, and owing to the strong anisotropy of the Co(II) ion, the local magnetic momenta do not perfectly align with respect to the field direction.

(c) CoCu(pbaOH)(H_2O)$_2$ (3). The $\chi_M T$ versus T plot for **3** is shown in Figure 3c. $\chi_M T$ is equal to 2.85 cm^3 K mol^{-1} at 300 K, presents a minimum at 110 K with $\chi_M T = 2.43$ cm^3 K mol^{-1}, then shows a very sharp increase with a break in the curve around 38 K. A very high maximum value of $\chi_M T$, equal to 555 cm^3 K mol^{-1}, is observed at 22 K.

The out-of-phase component of the susceptibility presents three distinct peaks. The maxima in the out-of-phase plot are proportional to the maximum energy absorption by the compound as its magnetization vector follows the alternating magnetic field. This occurs when the correlation length is the largest possible for this phase, i.e. infinite.[31] Hence, the three maxima may correspond to three ferromagnetic phases of the same compound. Alternatively, the experiment is effectively measuring three different spin−lattice relaxation processes within the same magnetic phase. The peak at the highest temperature occurs at 38 K, and is taken to be the critical temperature since at all temperatures below $T_c = 38$ K the sample exhibits a spontaneous magnetization. The other two peaks occur at 34 and 13 K.

The cycled magnetization versus field behavior for compound **3** at 2 K is displayed in Figure 5c. The coercive field is found to be as large as 5.66 × 10^3 Oe. As for **2**, the saturation magnetization for **3** is not reached yet at 50 kOe.

Once both compounds **2** and **3** have been allowed to stand in air for *ca.* 2 days, their magnetic behaviors become identical to that of compound **1**, and the process of dehydration may be repeated. Rehydration can also be achieved by adding the dehydrated compounds to water followed by filtration and drying as given in the synthesis details above.

Discussion and Conclusion

In chain compounds, the three-dimensional effects are governed by the interchain interactions, which are difficult to control. Very subtle structural changes may induce a crossover between three-dimensional antiferro- and ferromagnetic ordering. Such a situation is found in the CoCu(pbaOH) compounds **1**−**3**. The structural changes arise from a partial dehydration of the compounds. Removing the two non-coordinated water molecules from CoCu(pbaOH)(H_2O)$_3$•2H_2O (**1**) results in a new chain compound (**2**) in which the relative positions of the chains within the lattice are modified. The dominant interactions between the ferrimagnetic chains are antiferromagnetic in **1** and ferromagnetic in **2**. This latter compound exhibits a three-dimensional ferromagnetic ordering. Removing a third water molecule, occupying the apical position in the copper coordination sphere of **2**, results in compound **3** in which a spontaneous magnetization is observed below $T_c = 38$ K. The origin of this third water molecule is confirmed by the change of color of the material during the dehydration process. Indeed, this change of color arises from the modification of the copper environment, from square pyramidal to square planar.[29] Probably the loss of this apical water molecule makes the chains closer to each other.

The crystal structure of **3** is not known, and several questions remain unsolved concerning this compound. However, the scheme we propose concerning the removal of the water molecules is strongly supported by the reversibility of the dehydration process. If the chains were broken during this process, such a reversibility could not be achieved. Further evidence in favor of our scheme is provided by the comparison of the X-ray powder patterns for **1**−**3**. These patterns are close to each other with a slight decrease of the unit cell size from **1** to **3**. We also carefully checked that the X-ray pattern of the material resulting from the rehydration of **3** is strictly identical to that of a freshly prepared sample of **1**. It must be pointed out that the two steps of the dehydration process, concerning the non-coordinated and apical water molecules, respectively, are probably not perfectly separable versus temperature, in contrast with what happens for the Mn(II)Cu(II) compounds **4**−**6**. Around 100 °C at ambient pressure, the apical water molecule begins to be removed while the non-coordinated water molecules are not entirely removed yet. This might explain several experimental facts, namely, (i) a slightly more than two water molecules per CoCu unit are found to be lost at the point T_2 of Figure 2, (ii) compound **2** is blue-purple, suggesting that the copper coordination sphere is already slightly modified with regard to **1**, and (iii) the M'' versus T plot for **2** in Figure 4b shows a weak bump around 34 K.

To the best of our knowledge, compound **3** is one of the molecular-based magnets exhibiting the strongest coercivity reported so far. The coercive field at 2 K is equal to 5.66×10^3 Oe. The key factor of this huge coercivity is obviously the magnetic anisotropy of the Co(II) ion in octahedral surroundings. The way the compound is obtained might also contribute to this behavior. Indeed, the coercivity is not an intrinsic property; it depends on structural factors like grain size and shape. In the present case, the dehydration process affording **3** probably creates many defects within the crystallites, favoring the pinning of the ferromagnetic domain walls.

The reversibility of the dehydration process for $CoCu(pbaOH)(H_2O)_3 \cdot 2H_2O$ is a very appealing aspect of this material. Both **2** and **3**, when exposed to the air, reabsorb water and transform back into the initial compound. Such a reversibility could allow these compounds to be used as active elements of sensors, if the critical temperatures were higher.

At this stage, it is fair to say that we are faced with a dilemma. The crossover between an antiferro- and a ferromagnetic ground state together with the reversibility of the process are intimately related to the low-dimensional nature of the compound and its molecular character. But there is a price to pay, namely the rather low critical temperatures. Designing a three-dimensional compound should result in an increase of these critical temperatures. Such an effect has been found in Prussian blue-like phases.[32−34] However, in the meantime, the peculiar properties arising from the molecular character can vanish, and the physical properties of the three-dimensional magnet risk becoming very similar to those of classical magnets, such as the ferrites.

The design of molecular-based magnets exhibiting very strong coercivities seems to us to be an important step in molecular magnetism. We would like to understand the origin of this coercivity in a more thorough manner. This requires single crystal measurements. Until now, we have not succeeded in growing single crystals of Co(II)Cu(II) compounds suitable for anisotropic measurements, but we are pursuing our efforts along this line, and are investigating other compounds of that kind.

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