

# Dramatic Modifications of Magnetic Properties through Dehydration–Rehydration Processes of the Molecular Magnetic Sponges $\text{CoCu}(\text{obbz})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ and $\text{CoCu}(\text{obze})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ , with $\text{obbz} = N,N'$ -Bis(2-carboxyphenyl)oxamido and $\text{obze} = N$ -(2-Carboxyphenyl)- $N'$ -(carboxymethyl)oxamido

Joulia Larionova,<sup>†</sup> Suvarna A. Chavan,<sup>†,‡</sup> J. V. Yakhmi,<sup>‡</sup> Anne Gulbrandsen Frøystein,<sup>§</sup> Jorunn Sletten,<sup>§</sup> Claude Sourisseau,<sup>||</sup> and Olivier Kahn<sup>\*,†</sup>

Laboratoire des Sciences Moléculaires, Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS No. 9048, 33608 Pessac, France, Chemistry Division, Bhabha Atomic Research Center, 400 085 Mumbai, India, Department of Chemistry, University of Bergen, 5007 Bergen, Norway, and Laboratoire de Spectroscopie Moléculaire et Cristalline, URA CNRS No. 124, Université de Bordeaux 1, 33405 Talence, France

Received June 12, 1997<sup>⊗</sup>

The two compounds  $\text{CoCu}(\text{obbz})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$  (**I**) and  $\text{CoCu}(\text{obze})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$  (**II**) have been synthesized, and their crystal structures have been determined at room temperature. Both compounds crystallize in the monoclinic system, space group  $P2_1/n$ . The lattice parameters are  $a = 7.8190(6)$  Å,  $b = 12.534(2)$  Å,  $c = 20.2770(10)$  Å,  $\beta = 97.306(6)^\circ$ , and  $Z = 4$  for  $\text{CoCu}(\text{obbz})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$  and  $a = 17.966(5)$  Å,  $b = 6.907(1)$  Å,  $c = 13.678(3)$  Å,  $\beta = 97.69(1)^\circ$ , and  $Z = 4$  for  $\text{CoCu}(\text{obze})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ . For both compounds, the structure consists of isolated  $\text{Co}^{2+}\text{Cu}^{2+}$  pairs (in which the metal ions are bridged by an oxamide group) and noncoordinated water molecules. A thermogravimetric analysis has been carried out. Three water molecules are removed at a temperature  $T_2$  (96 °C for **I** and 120 °C for **II**), and five water molecules are removed at a temperature  $T_3$  (205 °C for **I** and 190 °C for **II**). When cooling down, the two compounds reabsorb water slowly and then return to the initial state. The dehydration–rehydration process is totally reversible, provided that the temperature does not exceed 275 °C. The magnetic properties of the starting materials, as well as the materials containing three water molecules and then one, have been investigated, both in the dc and ac modes. The two starting materials,  $\text{CoCu}(\text{obbz})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CoCu}(\text{obze})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ , possess a nonmagnetic ground state. The compounds  $\text{CoCu}(\text{obbz})(\text{H}_2\text{O})_3$  and  $\text{CoCu}(\text{obze})(\text{H}_2\text{O})_3$  behave as one-dimensional ferrimagnets without long-range magnetic ordering down to 2 K. The compounds  $\text{CoCu}(\text{obbz})(\text{H}_2\text{O})$  and  $\text{CoCu}(\text{obze})(\text{H}_2\text{O})$ , finally, also behave as ferrimagnets, but with a long-range magnetic ordering occurring at 25 and 20 K, respectively. Upon rehydration, the compounds return to the initial state with a nonmagnetic ground state. Infrared and Raman vibrational spectroscopies have been used to obtain further insights into the structural modifications accompanying the removal and the uptake of water molecules.

## Introduction

A few decades ago the distinction between solid state chemistry looking toward materials sciences and molecular chemistry looking toward reactivity, homogeneous catalysis, or life sciences was well pronounced. For some time, a molecular material science has existed. Among its achievements one can mention molecular conductors and superconductors, liquid crystals, molecular systems active in nonlinear optics, and more recently molecule-based magnets. The first molecular compounds exhibiting a spontaneous magnetization below a certain critical temperature were reported in 1967.<sup>1,2</sup> It was however only during the 1980s that the field of molecule-based magnets has developed rapidly, and today a large variety of such compounds are known.<sup>3–10</sup> In many cases, these compounds

contain two kinds of spin carriers, either two different metals ions<sup>11–20</sup> or a metal ion and an organic radical.<sup>21–28</sup> In at least two cases, three spin carriers are involved.<sup>29–31</sup>

<sup>†</sup> Institut de Chimie de la Matière Condensée de Bordeaux.

<sup>‡</sup> Bhabha Atomic Research Center.

<sup>§</sup> University of Bergen.

<sup>||</sup> Université de Bordeaux 1.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, December 1, 1997.

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One of the questions the people working in the field of molecular materials are faced with may be expressed as follows: The synthetic procedures leading to molecular materials are obviously totally different from those leading to more classical solid state materials. However, once these materials are obtained, are there still some differences according to whether they arise from molecular or solid state chemistry? In the field of magnetic materials, it has already been emphasized that the main originality of the molecular compounds arises from the fact that they are usually weakly colored while the classical magnets are opaque. Several groups including ours are presently investigating the optical and photophysical properties of molecular magnetic materials.<sup>32,33</sup> One of the important issues along this line would be to detect a synergy between optical (or photophysical) and magnetic properties.

Here, we are concerned by another specificity of molecular materials, namely the softness of their crystal lattices as compared to ionic or metallic lattices. We will show that it is possible to modify dramatically and reversibly the magnetic properties of molecular compounds through mild dehydration–rehydration processes. More precisely, this paper describes first the crystal structures and the magnetic properties of the bimetallic compounds  $\text{CoCu}(\text{obbz})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$  (**I**) and  $\text{CoCu}(\text{obze})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$  (**II**), where obbz stands for *N,N'*-bis-(carboxymethyl)oxamido and obze for *N*-(2-carboxymethyl)-*N'*-(carboxymethyl)oxamido, and then the reversible transformation between paramagnetic and ferromagnetic states as the compounds are successively dehydrated and rehydrated.

To save space, we will detail the results obtained with the  $\text{CoCu}(\text{obbz})$  compounds and will mention much more briefly those obtained with the  $\text{CoCu}(\text{obze})$  compounds, pointing out the few differences between the two systems. A preliminary report of a long-range ordering in compound **I** after dehydration has already appeared.<sup>34</sup>

## Experimental Section

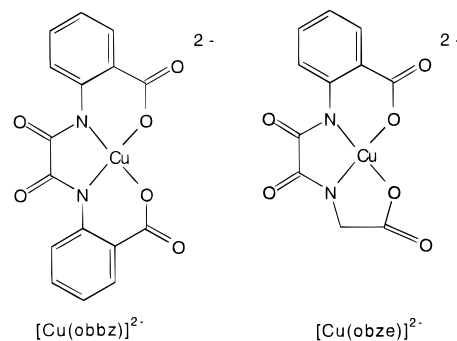
**Syntheses.** The organic molecules  $\text{H}_4\text{obbz}$  and  $\text{H}_4\text{obze}$  as well as the copper(II) precursors  $\text{Na}_2[\text{Cu}(\text{obbz})] \cdot 4\text{H}_2\text{O}$  and  $\text{Na}_2[\text{Cu}(\text{obze})] \cdot 2\text{H}_2\text{O}$  were synthesized as already described.<sup>35,36</sup> The structures of the two

**Table 1.** Crystallographic Data for  $\text{CoCu}(\text{obbz})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$  (**I**) and  $\text{CoCu}(\text{obze})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$  (**II**)

	<b>I</b>	<b>II</b>
empirical formula	$\text{C}_{16}\text{H}_{20}\text{CoCuN}_2\text{O}_{12}$	$\text{C}_{11}\text{H}_{18}\text{CoCuN}_2\text{O}_{12}$
fw	554.81	492.75
temp/K	293(1)	293(1)
$\lambda/\text{\AA}$	0.71073	0.71073
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
$a/\text{\AA}$	7.8190(6)	17.966(5)
$b/\text{\AA}$	12.534(2)	6.907(1)
$c/\text{\AA}$	20.2770(10)	13.678(3)
$\beta/\text{deg}$	97.306(6)	97.69(1)
$V/\text{\AA}^3$	1971.1(4)	1682(1)
Z	4	4
$\rho(\text{calc})/\text{g cm}^{-3}$	1.870	1.94
$\mu/\text{mm}^{-1}$	1.992	2.319
R1 [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.034	0.059
wR [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.070	0.058

<sup>a</sup> For compound **I**:  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ ;  $w = 1/\sigma^2(F_o^2) + (0.0342P)^2 + 0.7008P$ , where  $P = [0.3333 \times (\text{maximum of } 0 \text{ or } F_o^2) + 0.6667F_c^2]$ . For compound **II**:  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR = \{ \sum [w(|F_o| - |F_c|)^2] / \sum [w|F_o|^2] \}^{1/2}$ ;  $w = 1/\sigma^2(F_o)$ , where  $\sigma(F) = \sigma(I) (ILP)^{-1/2}$  and  $\sigma(I) = [\sigma_c^2 + (0.02F^2)^2]^{1/2}$ .

dianions  $[\text{Cu}(\text{obbz})]^{2-}$  and  $[\text{Cu}(\text{obze})]^{2-}$  are schematized as follows:



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$\text{CoCu}(\text{obbz})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$  (**I**) was synthesized as follows. A 20 mL portion of an aqueous solution containing  $5 \times 10^{-4}$  mol (0.145 g) of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was slowly added to 200 mL of a freshly filtered aqueous solution containing  $5 \times 10^{-4}$  mol (0.22 g) of  $\text{Na}_2[\text{Cu}(\text{obbz})] \cdot 4\text{H}_2\text{O}$ . A pale green-gray precipitate appeared. It was filtered off, washed with water, and dried in a desiccator containing silica gel. Anal. Calc for  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_{12}\text{CoCu}$  (**I**): C, 34.64; H, 3.63; N, 5.05; Co, 10.62; Cu, 11.45. Found: C, 35.02; H, 3.59; N, 4.85; Co, 10.42; Cu, 11.29.  $\text{CoCu}(\text{obbz})(\text{H}_2\text{O})_3$  and  $\text{CoCu}(\text{obbz})(\text{H}_2\text{O})$  were obtained by heating under vacuum the starting material to 96 and 205 °C, respectively. Well-shaped single crystals were obtained by slow diffusion in an H-shaped tube of two  $10^{-3}$  molar aqueous solutions containing  $\text{Na}_2[\text{Cu}(\text{obbz})] \cdot 4\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , respectively.  $\text{CoCu}(\text{obze})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$  (**II**) was prepared in a similar way, using  $\text{Na}_2[\text{Cu}(\text{obze})] \cdot 2\text{H}_2\text{O}$  as a precursor. Anal. Calc for  $\text{C}_{11}\text{H}_{18}\text{N}_2\text{O}_{12}\text{CoCu}$  (**II**): C, 26.81; H, 3.68; N, 5.69; Co, 11.96; Cu, 12.90. Found: C, 26.99; H, 3.76; N, 5.62; Co, 12.02; Cu, 12.81.

**X-ray Structure Determination and Refinement.** Diffraction data were collected at 293 K with an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Crystal parameters and refinement results are compiled in Table 1. Cell dimensions were determined on the basis of the setting angles of 25 reflections in the  $2\theta$  range 29–42 and 19–35° for **I** and **II**, respectively. A total of 3828 (**I**) and 2970 (**II**) reflections within  $2\theta = 50^\circ$  were recorded using the  $\omega/2\theta$  scan technique. Three reference reflections monitored throughout the data collection showed a moderate decay of 3% on average for **I** and no significant decay for **II**. The data were corrected for Lorentz and polarization effects and for linear decay.

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**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for CoCu(obbz)(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O (I)

Bond Lengths			
Cu—O(3)	1.905(2)	O(2)—C(2)	1.250(4)
Cu—O(4)	1.909(2)	O(3)—C(5)	1.283(4)
Cu—N(1)	1.934(3)	O(4)—C(12)	1.266(4)
Cu—N(2)	1.935(3)	O(5)—C(5)	1.250(4)
Co—O(10)	2.053(3)	O(6)—C(12)	1.259(4)
Co—O(1)	2.065(2)	N(1)—C(1)	1.318(4)
Co—O(2)	2.065(2)	N(1)—C(3)	1.416(4)
Co—O(7)	2.107(3)	N(2)—C(2)	1.325(4)
Co—O(9)	2.118(3)	N(2)—C(10)	1.423(4)
Co—O(8)	2.121(4)	C(1)—C(2)	1.543(5)
O(1)—C(1)	1.250(4)		
Bond Angles			
O(3)—Cu—O(4)	85.21(10)	O(2)—Co—O(7)	90.39(13)
O(3)—Cu—N(1)	93.61(10)	O(10)—Co—O(9)	89.39(13)
O(4)—Cu—N(1)	176.82(11)	O(1)—Co—O(9)	175.97(12)
O(3)—Cu—N(2)	173.70(12)	O(2)—Co—O(9)	99.11(11)
O(4)—Cu—N(2)	93.09(11)	O(7)—Co—O(9)	88.79(14)
N(1)—Cu—N(2)	88.40(11)	O(10)—Co—O(8)	89.3(2)
O(10)—Co—O(1)	93.63(12)	O(1)—Co—O(8)	91.68(12)
O(10)—Co—O(2)	170.51(13)	O(2)—Co—O(8)	95.5(2)
O(1)—Co—O(2)	78.09(9)	O(7)—Co—O(8)	172.48(14)
O(10)—Co—O(7)	85.6(2)	O(9)—Co—O(8)	85.69(13)
O(1)—Co—O(7)	94.10(12)		

Absorption correction for **I** was done on the basis of  $\psi$ -scan measurements using seven reflections,<sup>37</sup> and that for compound **II**, by the Gaussian integration method.

Structure **I** was solved by direct methods; for compound **II**, the coordinates of the isomorphous MnCu compound were used as a starting point.<sup>36</sup> Full-matrix least-squares refinements were carried out, for **I** based on  $F^2$  and for **II** based on  $F$ . Non-hydrogen atoms were anisotropically refined. Hydrogen atoms bonded to carbon were included at idealized calculated positions. Hydrogen atoms bonded to oxygen atoms were located in difference Fourier maps and were isotropically refined. In the case of **II**, hydrogen atoms belonging to the noncoordinated water molecules as well as to two of the coordinated water molecules could not be unambiguously located. An extinction parameter was included in the final refinement cycles. In the case of **I**, the refinement, based on  $F^2$  and including all reflections, converged at  $R1 = 0.060$ ,  $wR2 = 0.081$ . The conventional  $R1$  factor including the 2544 reflections with  $I > 2\sigma(I)$  is 0.034. For **II**, the refinement, based on  $F$  and including 1757 reflections with  $I > 2\sigma(I)$ , converged at  $R1 = 0.059$ ,  $R_w = 0.058$ .

For structure **I**, the data reduction was done with the XCAD program<sup>38</sup> and all other calculations were performed with the SHELXS-86, SHELXL-93, and XPL programs.<sup>39</sup> For structure **II**, all calculations were carried out using the Enraf-Nonius Structure Determination Programs.<sup>40</sup> Selected bond lengths are listed in Table 2, and selected bond angles, in Table 3.

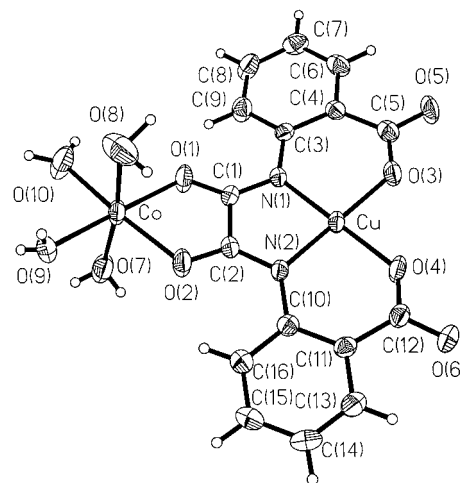
**Thermogravimetric Measurements.** These were carried out with a Setaram TAGDSC apparatus, in the range 20–250 °C under a nitrogen atmosphere.

**Magnetic Measurements.** These were performed with a Quantum Design MPMS-5S SQUID magnetometer, working in both the dc and the ac modes, in the temperature range 2–300 K, and in the 0–50 kOe field range. The temperature dependences of the ac magnetic susceptibility were recorded at a field alternation frequency of 125 Hz and a drive amplitude of 1 Oe. The chemical compositions of all compounds under magnetic investigation were checked.

**Infrared and Raman Spectra.** All samples were handled in a dry-air glovebag atmosphere. The mull infrared spectra (4000–400 cm<sup>-1</sup>)

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for CoCu(obbz)(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O (II)

Bond Lengths			
Cu—O(3)	1.976(6)	O(2)—C(2)	1.24(1)
Cu—O(4)	1.869(6)	O(3)—C(4)	1.28(1)
Cu—N(1)	1.893(7)	O(4)—C(7)	1.31(1)
Cu—N(2)	1.930(7)	O(5)—C(4)	1.25(1)
Co—O(1)	2.106(6)	O(6)—C(7)	1.25(1)
Co—O(2)	2.060(6)	N(1)—C(1)	1.27(1)
Co—O(7)	2.130(8)	N(1)—C(3)	1.45(1)
Co—O(8)	2.103(8)	N(2)—C(2)	1.36(1)
Co—O(9)	2.084(7)	N(2)—C(5)	1.42(1)
Co—O(10)	2.103(6)	C(1)—C(2)	1.54(1)
O(1)—C(1)	1.25(1)		
Bond Angles			
O(3)—Cu—O(4)	95.1(3)	O(2)—Co—O(7)	95.2(3)
O(3)—Cu—N(1)	82.9(3)	O(2)—Co—O(8)	88.4(3)
O(3)—Cu—N(2)	167.5(3)	O(2)—Co—O(9)	90.0(3)
O(4)—Cu—N(1)	177.2(4)	O(2)—Co—O(10)	176.0(4)
O(4)—Cu—N(2)	97.2(3)	O(7)—Co—O(8)	176.0(3)
N(1)—Cu—N(2)	84.8(3)	O(7)—Co—O(9)	87.4(3)
O(1)—Co—O(2)	79.4(2)	O(7)—Co—O(10)	88.6(3)
O(1)—Co—O(7)	88.6(3)	O(8)—Co—O(9)	90.8(3)
O(1)—Co—O(8)	93.9(3)	O(8)—Co—O(10)	87.8(3)
O(1)—Co—O(9)	168.2(3)	O(9)—Co—O(10)	91.6(3)
O(1)—Co—O(10)	99.4(3)		

**Figure 1.** The molecular unit CoCu(obbz)(H<sub>2</sub>O)<sub>4</sub> in compound **I**. Thermal ellipsoids are plotted at the 70% probability level.

were recorded from polycrystalline samples dispersed in Nujol or Fluorolube oil on a Digilab (Bio-Rad, DA3) interferometer with a resolution of 2 cm<sup>-1</sup>, using CaF<sub>2</sub> or CsI flat optical windows. The Raman spectra (2000–50 cm<sup>-1</sup>) were recorded in the backscattering geometry, using an optical multichannel instrument (OMARS 89 from DILOR) in conjunction with a confocal microscope (100× objective) and a liquid-nitrogen-cooled CCD detector (EG and G, PARC model 1530C). The power of the incident laser radiation (514.5 nm) was minimized (5–10 mW) in order to avoid any thermal or photochemical effect, and the laser beam was focused on polycrystalline grains through the wall of sealed Pyrex tubes. The wavenumber measurements ( $\pm 1$  cm<sup>-1</sup>) were calibrated using plasma lines.

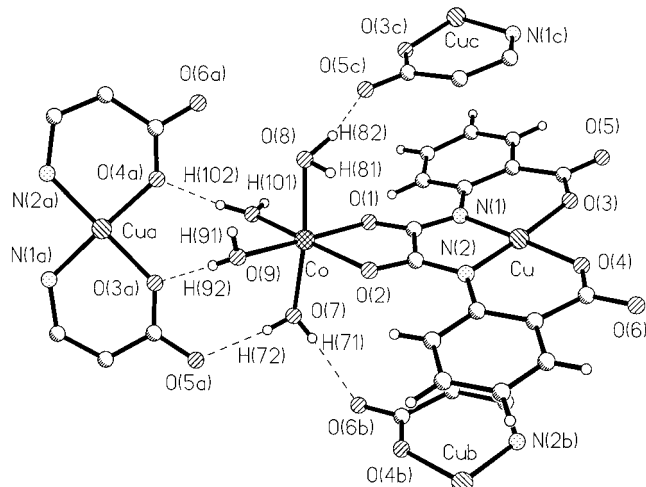
## Description of the Structures

**CoCu(obbz)(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O (I).** The structure is isomorphous with that of NiCu(obbz)(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O already described.<sup>35</sup> It consists of neutral CoCu(obbz)(H<sub>2</sub>O)<sub>4</sub> units (see Figure 1) and noncoordinated water molecules. The Co atom has a somewhat distorted octahedral environment with two oxygen atoms of the oxamido group and four water molecules in the coordination sphere. All Co—O bond lengths are somewhat longer than the corresponding Ni—O bond lengths in the isomorphous compound. It is interesting to note that Co—O(10) is significantly

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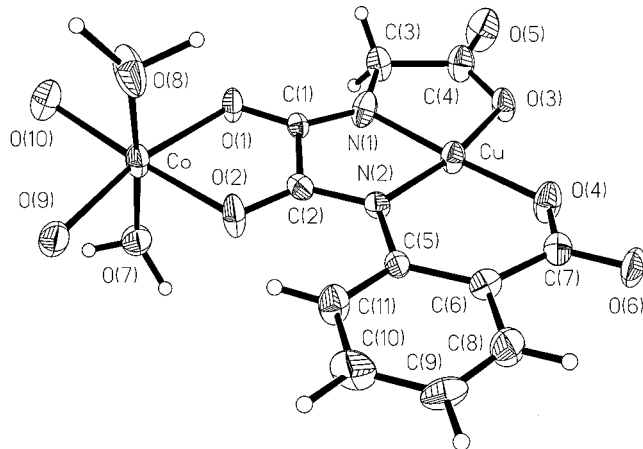
**Figure 2.** Hydrogen bonding involving the coordinated water molecules in compound **I**. The reference molecule is in position  $x, y, z$ . Symmetry operations:  $a = -1/2 + x, 3/2 - y, -1/2 + z$ ;  $b = 1 - x, 1 - y, 1 - z$ ;  $c = 1 - x, 2 - y, 1 - z$ .

shorter than the other Co—O(water) bonds; this feature was also evident in the Ni compound. The Cu environment may be described as square planar with a slight tetrahedral distortion, the axial positions being screened by carbon atoms in neighboring molecules related by inversion centers with Cu—C(7)( $1 - x, 2 - y, 1 - z$ ) = 3.416(4) Å and Cu—C(15)( $1 - x, 1 - y, 1 - z$ ) = 3.236(4) Å. The dihedral angles between the bridging oxamido group and the Cu and Co equatorial planes are 7.89 and 8.55°, respectively.

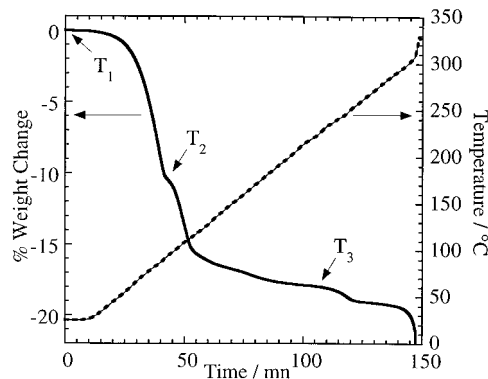
The Co—Cu distance within the binuclear unit is 5.295(1) Å. The shortest intermolecular distance between metal atoms occurs between molecules related by the  $n$ -glide, Co—Cu( $-1/2 + x, 3/2 - y, -1/2 + z$ ) being 5.109(1) Å. Across inversion centers there are Cu—Cu distances of 6.203(1) Å [Cu—Cu( $1 - x, 1 - y, 1 - z$ )] and 6.695(1) Å [Cu—Cu( $1 - x, 2 - y, 1 - z$ )], and between molecules related by screw axes Co—Co( $1/2 - x, 1/2 + y, 1/2 - z$ ) is 6.417(1) Å.

The molecules are connected through an extensive network of hydrogen bonds (see Figure 2). In particular, one may notice that molecules related by the  $n$ -glide (shortest intermolecular Co—Cu) are laced into chains through three hydrogen bonds involving coordinated water in one molecule and carboxylate groups of the next molecule: O(7)—H(72)—O(5) $a$ , O(9)—H(92)—O(3) $a$ , and O(10)—H(102)—O(4) $a$  (where  $a$  signifies symmetry operation  $-1/2 + x, 3/2 - y, -1/2 + z$ ). Axially coordinated water molecules also form hydrogen bonds to carboxylate groups in molecules related by centers of symmetry: O(7)—H(71)—O(6) $b$  and O(8)—H(82)—O(5) $c$  (where  $b$  and  $c$  denote symmetry operations  $1 - x, 1 - y, 1 - z$  and  $1 - x, 2 - y, 1 - z$ , respectively).

**CoCu(obze)(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O (II).** The structure is isomorphous with that of MnCu(obze)(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O.<sup>36</sup> It consists of CoCu(obze)(H<sub>2</sub>O)<sub>4</sub> units and noncoordinated water molecules (see Figure 3). The Co environment is very similar to that found for CoCu(obbz)(H<sub>2</sub>O)<sub>4</sub>. The Cu atom is coordinated to two oxamido nitrogen atoms and two carboxylato oxygen atoms in a slightly distorted square planar arrangement. The axial positions of Cu are screened by the proximity of the phenyl rings of centrosymmetrically related molecules with Cu—C(6)-(1 -  $x, 1 - y, 2 - z$ ) and Cu—C(10)(1 -  $x, 1 - y, 2 - z$ ) equal to 3.31 Å. The dihedral angles between the bridging oxamido group and the Cu and Co equatorial planes are 6.9 and 6.0°, respectively.



**Figure 3.** The molecular unit CoCu(obze)(H<sub>2</sub>O)<sub>4</sub> in compound **II**. Thermal ellipsoids are plotted at the 70% probability level.



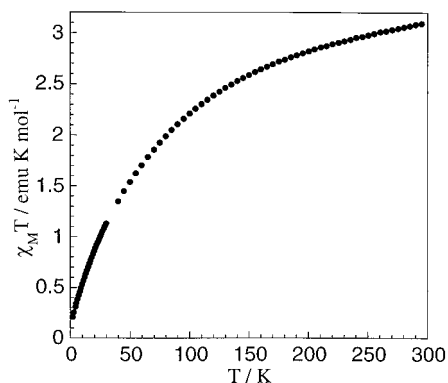
**Figure 4.** Overlay of temperature and percentage weight loss versus time, obtained by a thermogravimetric study of CoCu(obbz)(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O (**I**).

The Co—Cu distance within the binuclear unit is 5.319(2) Å. The shortest Cu—Cu intermolecular distances occur between molecules related by inversion centers, Cu—Cu( $1 - x, 1 - y, 2 - z$ ) = 4.612(2) Å alternating with Cu—Cu( $1 - x, -y, 2 - z$ ) = 5.931(2) Å along the  $b$  axis. The shortest Co—Cu intermolecular distance is found between molecules related by the  $n$ -glide, Cu—Co( $1/2 + x, 1/2 - y, 1/2 - z$ ) = 5.838 Å. Furthermore, pairs of centrosymmetrically related Co atoms are separated by 5.448(2) Å [Co—Co( $1 - x, -y, 1 - z$ )], the two coordination spheres being linked through hydrogen bonds between O(7) and O(10). The O(6) atom is hydrogen bonded to the oxygens of the axially coordinated water molecules O(7) and O(8) in molecular units one unit cell apart along the  $b$  axis. The Co—O(6)(1 -  $x, -y, 2 - z$ ) and Co—O(6)(1 -  $x, 1 - y, 2 - z$ ) distances are only 3.951 and 3.987 Å.

For both compounds **I** and **II**, the X-ray powder patterns are strongly modified upon dehydration, but the compounds remain crystalline. Upon rehydration, the patterns return to those of the starting compounds, whose crystal structures are described above.

### Thermogravimetric Analyses

**CoCu(obbz)(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O (I).** Figure 4 shows the overlay of time versus temperature and time versus percentage change in weight for a sample of CoCu(obbz)(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O. Initially, the temperature was increased at the rate of 30 °C/h, giving a region of rapid weight loss between 21 °C (point T<sub>1</sub>) and 96 °C (point T<sub>2</sub>). The percentage weight loss at T<sub>2</sub> corresponds to three molecules of water per CoCu unit. As the temperature was increased further, a second inflection point (T<sub>3</sub>) was



**Figure 5.**  $\chi_M T$  versus  $T$  plot for  $\text{CoCu(obbz)(H}_2\text{O)}_4 \cdot 2\text{H}_2\text{O}$  (**Ia**).

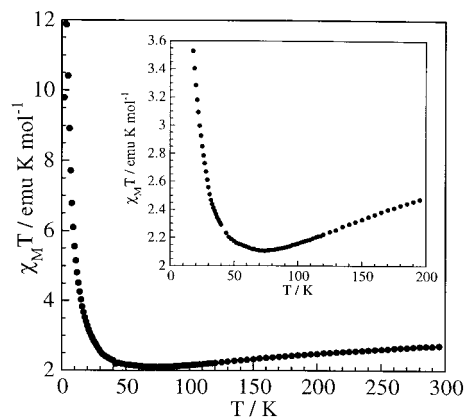
observed around 200 °C, corresponding to a total loss of five molecules of water. Increasing again the temperature up to ca. 275 °C resulted in a very progressive loss of half a water molecule, before the compound decomposed irreversibly. If the heating was stopped at  $T_3$ , the sample began to reabsorb water slowly. The degree of hydration after 24 h depended on the humidity of atmosphere. If the sample was kept at room temperature in the close vicinity of a beaker of water, the rehydration was complete, and we obtained a material whose chemical composition, structure, and physical properties (vide infra) were strictly identical to those of the starting material. The dehydration–rehydration process could be repeated as many times as desired without any detectable fatigability of the material, provided that the temperature never exceeded 275 °C.

**CoCu(obze)(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O (II).** The thermogravimetric behavior of  $\text{CoCu(obze)(H}_2\text{O)}_4 \cdot 2\text{H}_2\text{O}$  is rather similar to that of the obbz derivative. The most noticeable differences are the following: (i) the  $T_2$  and  $T_3$  temperatures are found at 120 and 190 °C, respectively; (ii) the rehydration process is much faster, so that the magnetic studies of the dehydrated compounds were performed with sample holders sealed under vacuum after heating.

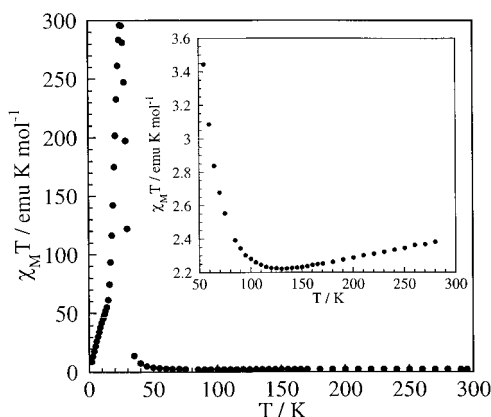
### Magnetic Properties

**The CoCu(obbz) System.** The magnetic studies were carried out on four compounds, namely the starting material (**Ia**), the material heated to 96 °C (**Ib**), the material heated to 205 °C (**Ic**), and finally the material fully rehydrated after thermal treatment (**Id**). Let us present successively the magnetic properties of each of these materials.

(a) **CoCu(obbz)(H<sub>2</sub>O)<sub>4</sub>·2H<sub>2</sub>O (Ia).** The temperature ( $T$ ) dependence of the dc molar magnetic susceptibility ( $\chi_M$ ) is shown in Figure 5 in the form of the  $\chi_M T$  versus  $T$  plot;  $\chi_M T$  is equal to 2.89 emu K mol<sup>-1</sup> at room temperature, decreases continuously as  $T$  is lowered, and reaches a value very close to zero at 2 K. This behavior is quite characteristic of an antiferromagnetically coupled  $\text{Co}^{2+}\text{Cu}^{2+}$  pair, with a nonmagnetic ground state. A very similar curve was obtained and quantitatively interpreted for  $\text{CoCu(obp)(H}_2\text{O)}_3 \cdot \text{H}_2\text{O}$  with obp =  $N,N'$ -(2-carboxyethyl)oxamido.<sup>41</sup> We will not repeat here the theoretical treatment and will limit ourselves to recall why the ground state is nonmagnetic at the first order.<sup>6,41,42</sup> The  $^4T_1$  ground state of  $\text{Co}^{2+}$  in cubic symmetry is split into three spin-quartet states in the rhombic symmetry observed for the compound. Each of these spin-quartet states is split further into two Kramers doublets. The antiferromagnetic interaction between the  $\text{Co}^{2+}$  Kramers doublet of lowest energy and the



**Figure 6.**  $\chi_M T$  versus  $T$  plot for  $\text{CoCu(obbz)(H}_2\text{O)}_3$  (**Ib**). The insert emphasizes the minimum in the  $\chi_M T$  versus  $T$  plot.



**Figure 7.**  $\chi_M T$  versus  $T$  plot for  $\text{CoCu(obbz)(H}_2\text{O)}$  (**Ic**). The insert emphasizes the minimum in the  $\chi_M T$  versus  $T$  plot.

$\text{Cu}^{2+}$  Kramers doublet gives rise to a singlet nonmagnetic ground state and a zero-field-split pseudotriplet magnetic excited state for the pair. One can also say that the ground Kramers doublet of  $\text{Co}^{2+}$  may be characterized by an  $S'_{\text{Co}} = 1/2$  effective local spin.<sup>6</sup> The antiferromagnetic interaction between  $S'_{\text{Co}}$  and  $S_{\text{Cu}} = 1/2$  leads to an  $S = 0$  ground pair state.

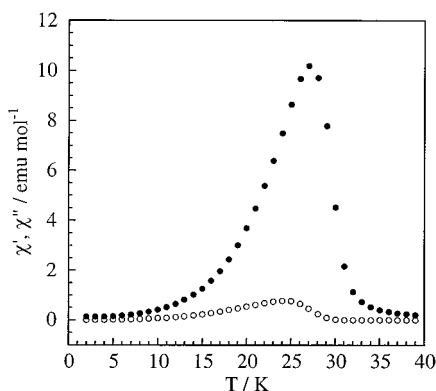
(b) **CoCu(obbz)(H<sub>2</sub>O)<sub>3</sub> (Ib).** The  $\chi_M T$  versus  $T$  curve for compound **Ib**, shown in Figure 6, is already deeply modified with regard to that of compound **Ia**;  $\chi_M T$  is equal to 2.70 emu K mol<sup>-1</sup> at 300 K, decreases very smoothly as  $T$  decreases, reaches a minimum value at 74 K, with  $\chi_M T = 2.12$  emu K mol<sup>-1</sup>, then increases as  $T$  is lowered further, and reaches a value of 12 emu K mol<sup>-1</sup> at 2 K. The minimum in the  $\chi_M T$  versus  $T$  curve is characteristic of ferrimagnetic behavior.<sup>6</sup> Through extended  $\text{Co}^{2+}\text{--Cu}^{2+}$  antiferromagnetic interactions the  $\text{Co}^{2+}$  magnetic moments tend to align along the field direction and the  $\text{Cu}^{2+}$  magnetic moments along the opposite direction. The compound, however, shows no long-range magnetic ordering down to 2 K; the out-of-phase ac magnetic susceptibility is zero in the whole 2–300 K temperature range.

(c) **CoCu(obbz)(H<sub>2</sub>O) (Ic).** The magnetic properties for this compound reveal not only a ferrimagnetic behavior but also a long-range magnetic ordering at  $T_c = 25$  K. The  $\chi_M T$  versus  $T$  curve is shown in Figure 7.  $\chi_M T$  is equal to 2.60 emu K mol<sup>-1</sup> at room temperature, decreases as  $T$  is lowered, presents a minimum at 130 K, with  $\chi_M T = 2.22$  emu K mol<sup>-1</sup>, and then increases very abruptly as  $T$  is lowered further. A very high maximum of  $\chi_M T$  is observed around 25 K, with  $\chi_M T = 300$  emu K mol<sup>-1</sup> (with an applied field of 10<sup>2</sup> Oe). The decrease of  $\chi_M T$  below 25 K is due to saturation effects.

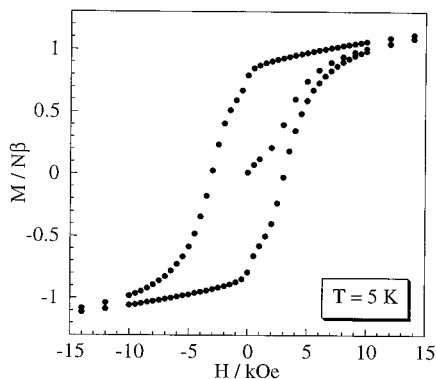
The onset of a long-range magnetic transition is confirmed by the temperature dependences of the in-phase,  $\chi'$ , and out-

(41) Gulbrandsen, A.; Sletten, J.; Nakatani, K.; Pei, Y.; Kahn, O. *Inorg. Chim. Acta* **1993**, 212, 271.

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**Figure 8.** Temperature dependence of the in-phase (●) and out-of-phase (○) ac molar magnetic susceptibilities for  $\text{CoCu(obbz)(H}_2\text{O)}$  (**Ic**).



**Figure 9.** Magnetic hysteresis loop at 5 K for  $\text{CoCu(obbz)(H}_2\text{O)}$  (**Ic**).

of-phase,  $\chi''$ , ac molar magnetic susceptibilities displayed in Figure 8; both  $\chi'$  and  $\chi''$  present a peak, at 27 and 25 K, respectively. The temperature of the maximum of  $\chi''$  does not depend on the frequency between 1 and  $10^3$  Hz. This compound, **Ic**, may be considered as a rather hard magnet. As a matter of fact, the field dependence of the magnetization at 5 K reveals a well-shaped hysteresis loop, with a coercive field of  $3.0 \times 10^3$  Oe (see Figure 9).

(d)  $\text{CoCu(obbz)(H}_2\text{O)}_4 \cdot 2\text{H}_2\text{O}$  (**Id**). This compound, obtained after thermal treatment up to 205 °C and complete rehydration, behaves magnetically exactly as the starting compound **Ia**, with  $\chi_M T$  tending to zero as  $T$  approaches absolute zero.

**CoCu(obze) System.** Very similar results were obtained concerning the magnetic properties of the  $\text{CoCu(obze)}$  compounds.  $\text{CuCo(obze)(H}_2\text{O)}_4 \cdot 2\text{H}_2\text{O}$  possesses a nonmagnetic ground state;  $\text{CuCo(obze)(H}_2\text{O)}_3$  behaves as a ferrimagnet without long-range ordering down to 2 K;  $\text{CuCo(obze)(H}_2\text{O)}$  also behaves as a ferrimagnet but exhibits a long-range magnetic ordering at  $T_c = 20$  K.

## Discussion

In this section, we will focus on the  $\text{CoCu(obbz)}$  system. Let us start the discussion by summing up what is already clear from the results described above. The reaction of  $[\text{Cu(obbz)}]^{2-}$  with  $\text{Co}^{2+}$  yields the binuclear species of formula  $\text{CoCu(obbz)(H}_2\text{O)}_4 \cdot 2\text{H}_2\text{O}$  with four water molecules in the cobalt coordination sphere and two additional noncoordinated water molecules. The ground state of the  $\text{Co}^{2+}\text{Cu}^{2+}$  pair is nonmagnetic at the first order. When this compound, **Ia**, is heated, three water molecules are removed; this removal is accompanied by a sort of polymerization process yielding a low-dimensional compound, **Ib**, with a ferrimagnetic behavior. Heating this compound further up to 200 °C results in the removal of two more

water molecules and a development of the polymerization process, yielding a ferrimagnetic material, **Ic**, which exhibits a long-range magnetic ordering at  $T_c = 25$  K, and a rather strong coercivity below  $T_c$ . What is quite remarkable is that the dehydration process is perfectly reversible. In a humid atmosphere, the molecule-based magnet **Ic** slowly reabsorbs water and transforms back into compound **Ia** with a nonmagnetic ground state.

Let us now try to go further, and to figure out the transformations leading to compounds **Ib** and **Ic**.

The first three water molecules which are removed are certainly the two noncoordinated water molecules along with one of the molecules linked to the cobalt atom, so that the formula of the compound can be written as  $\text{CoCu(obbz)(H}_2\text{O)}_3$ . A very similar compound of formula  $\text{CoCu(obp)(H}_2\text{O)}_3$ , with  $\text{obp} = N,N'$ -bis(2-carboxyethyl)oxamido, does exist.<sup>40</sup> This compound has a chain structure. The cobalt atom is surrounded by six oxygen atoms, two of them coming from the oxamido bridge, three from water molecules, and the sixth one from the carboxylato group of a neighboring unit. In  $\text{CoCu(obp)(H}_2\text{O)}_3$ , the  $\text{Co}^{2+}\text{--Cu}^{2+}$  interaction through the carboxylato bridge was found to be too weak to give rise to the ferrimagnetic regime with a minimum in the  $\chi_M T$  versus  $T$  curve. However, it has been shown that the magnitude of this interaction may dramatically depend on the configuration around this carboxylato bridge.<sup>43–45</sup>

The situation is more complicated as far as compound **Ic** is concerned. This compound has only one water molecule in the cobalt coordination sphere. This could suggest that the  $\text{Co}^{2+}$  ion is in a tetrahedral environment. Such a hypothesis, however, may be ruled out. Indeed, compound **Ic** is a rather hard magnet. Therefore, the  $\text{Co}^{2+}$  ion in **Ic** is a magnetically anisotropic spin carrier. This would not be the case if this ion was in a tetrahedral environment with a  $^4\text{A}_2$  ground state, without first-order orbital momentum. We must admit that the  $\text{Co}^{2+}$  ion in **Ic** is in an octahedral environment, as it was in **Ia** and **Ib**. This is possible if the two water molecules which are removed when passing from **Ib** to **Ic** are replaced by two carboxylato oxygen atoms belonging to neighboring chains, resulting in a two- or a three-dimensional network. Let us note here that the electronic absorption spectrum usually allows one to distinguish between octahedral and tetrahedral  $\text{Co}^{2+}$  chromophores. In the present case, the spectrum in the visible range is dominated by the d–d bands of the  $\text{Cu}^{2+}$  chromophore and the bands arising from  $\text{Co}^{2+}$  cannot be assigned.

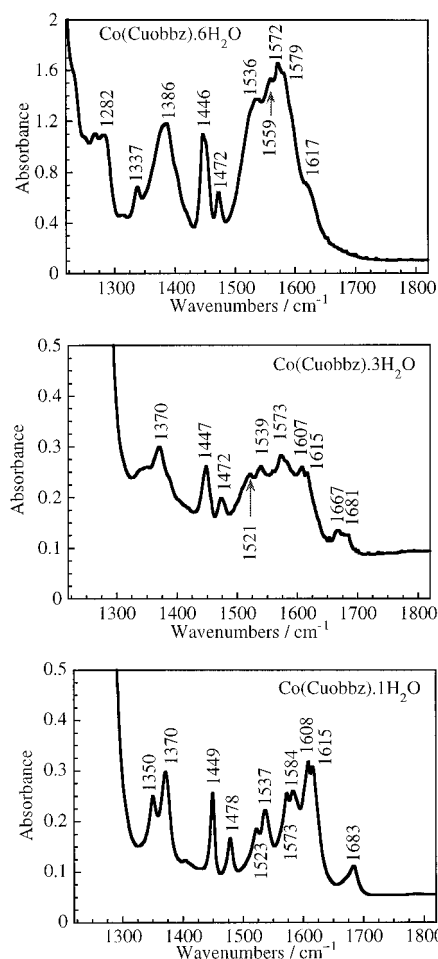
Let us now examine whether the infrared and Raman spectroscopy data are in line with the propositions above. We first look at the infrared data in the 1300–1800  $\text{cm}^{-1}$  range, corresponding to the  $\nu_{\text{COO}}$  vibrations.<sup>46</sup> The spectra of **Ia**, **Ib**, and **Ic** are compared in Figure 10. The spectrum of **Ia** shows several intense and broad bands in the 1550–1620  $\text{cm}^{-1}$  range which can be assigned to the antisymmetric  $\nu_{\text{COO}}$  vibrations of the monodentate carboxylato groups. For **Ib**, the relative intensities of these bands decrease and new bands appear in the 1600–1620  $\text{cm}^{-1}$  range. Those probably correspond to antisymmetric  $\nu_{\text{COO}}$  vibrations of bridging carboxylato groups ( $\text{Cu--O--C--O--Co}$ ). Another difference between the spectra of **Ia** and **Ib** is the appearance of new bands in the 1660–1690

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(44) Nakatani, K.; Sletten, J.; Halut-Desporte, S.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1991**, *30*, 164.

(45) Kahn, O.; Pei, Y.; Nakatani, K.; Journaux, Y. *New. J. Chim.* **1992**, *16*, 269.

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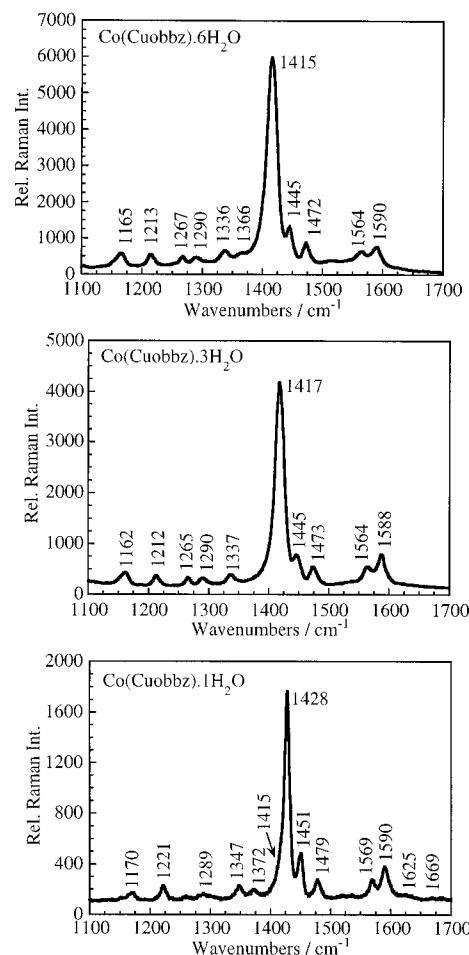


**Figure 10.** Comparison of the infrared spectra of compounds **Ia**, **Ib**, and **Ic** in the 1300–1800  $\text{cm}^{-1}$  wavenumber range.

$\text{cm}^{-1}$  range. Their higher energy suggests that they arise from very asymmetrical carboxylato groups, with the same oxygen atom linked to both Co and Cu atoms. The relative intensities of these two groups of bands increase further upon passing from **Ib** to **Ic**, which might be related to the formation of two Co–O bonds involving both bridging and strongly asymmetrical carboxylato groups at the expense of two Co–H<sub>2</sub>O bonds.

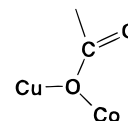
The Raman spectra in the same wavenumber range are compared in Figure 11. The spectrum of **Ia** is dominated by the signal at 1415  $\text{cm}^{-1}$  assignable to the symmetric  $\nu_{\text{COO}}$  vibrations of monodentate carboxylato groups. Upon dehydration, this band is shifted toward higher energy and appears at 1428  $\text{cm}^{-1}$  for **Ic**. This wavenumber agrees with what is expected for the symmetric  $\nu_{\text{COO}}$  vibration of bridging carboxylato groups. One can also notice that a weak signal around 1415  $\text{cm}^{-1}$  is still present in the spectrum, as a low-energy shoulder of the signal at 1428  $\text{cm}^{-1}$ . Let us finally mention that the perfect reversibility of the dehydration–rehydration process was checked again from the Raman spectra by accommodating a tiny air leak in the sealed tube containing **Ic**. The shift of the  $\nu_{\text{COO}}$  mode from 1428 down to 1415  $\text{cm}^{-1}$  was observed, along with the variation of the half-bandwidth from 10 to ca. 22  $\text{cm}^{-1}$ .

To conclude this section, let us summarize what precedes. It is quite reasonable to suggest that compound **Ib** has a chain structure reminiscent of that found for  $\text{CoCu}(\text{obp})(\text{H}_2\text{O})_3$  and behaves as a one-dimensional ferrimagnet without long-range ordering. In **Ic**, the chains would not be isolated from each other anymore but would associate to afford a network of higher dimensionality. The monodentate carboxylato groups of a chain

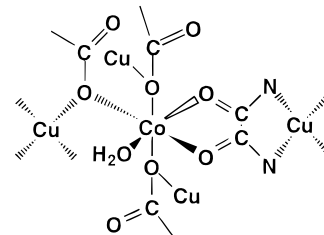


**Figure 11.** Comparison of the Raman spectra of compounds **Ia**, **Ib**, and **Ic** in the 1100–1700  $\text{cm}^{-1}$  wavenumber range.

would create Co–O bonds involving  $\text{Co}^{2+}$  ions of neighboring chains. The presence of infrared bands around 1680  $\text{cm}^{-1}$  suggests that the coordination would be as



If it was so, the  $\text{Co}^{2+}$  ion in **Ic** would be surrounded by six oxygen atoms, one arising from a water molecule, two from the oxamido group, one from a carboxylato group with an atom of the type O(5) or O(6) (see Figure 1), and two from carboxylato groups with atoms of the type O(3) and O(4), schematized below as follows:



Such a description, however, does not explain why the bands around 1680  $\text{cm}^{-1}$  are already visible in the infrared spectrum of **Ib**. Perhaps, at 96 °C, compound **Ic** begins to form, or more likely the structure of **Ib** is more disordered than suggested

above, with some  $\text{Co}^{2+}$  ions possessing oxygen atoms of the type O(3) or O(4) in their coordination spheres.

At this stage, we wish to mention that this hydration–dehydration process accompanied by a paramagnetic–ferromagnetic transformation has already been observed, in particular for the system  $(\text{RNH}_3)_2\text{CrX}_4-(\text{RNH}_3)_2[\text{CrX}_4(\text{H}_2\text{O})_2]$ .<sup>47</sup>

### Conclusion

The two compounds, **I** and **II**, investigated in this paper may be considered as molecular magnetic sponges. They can reversibly release and absorb five water molecules, a process which is accompanied by a dramatic change of magnetic properties. When the sponges are hydrated, or wet, they exhibit a nonmagnetic ground state;  $\chi_{\text{M}}T$  tends to zero as  $T$  approaches absolute zero. When the sponges are dehydrated, or dry, they exhibit a spontaneous magnetization below critical temperatures of 25 and 20 K, respectively. The reversibility of the process seems to us to be the most remarkable finding of this work. It

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(47) We thank the reviewer who brought this interesting system to our attention.

is due to the softness of these crystal lattices. The Co–O bonds can be broken and created without destroying the essence of the molecular architecture. Dehydration increases the magnetic dimensionality from zero to 2 or 3; rehydration decreases this dimensionality.

Sometimes, we are asked to describe the properties of molecular magnetic materials as compared to classical solid-state magnetic materials. The phenomena reported in this paper certainly represent striking properties of molecule-based matter.

**Acknowledgment.** This work was carried out under Project No. 1308-G funded by the Indo-French Center for the Promotion of Advanced Research (IFCPAR). The authors thank R. Cavagnat for his technical assistance in Raman measurements.

**Supporting Information Available:** Tables of X-ray experimental details, atomic coordinates, anisotropic thermal parameters for the non-hydrogen atoms, bond lengths and angles, and hydrogen bonds for compounds **I** and **II** (18 pages). Ordering information is given on any current masthead page.

IC970719G