

## Reversible Structural Transformation and Drastic Magnetic Change in a Copper Hydroxides Intercalation Compound

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There is a considerable interest in the packing and dynamics of long-chain polymethylene compounds intercalated in layered materials, because of their relevance to functionalities of biological membranes, liquid crystals, etc.<sup>1,2</sup> Some of the materials are known to exhibit characteristic transformations; such as *trans/gauche* transitions of the alkyl chains and monolayer/bilayer phase transitions, which are triggered by heat or soaking in solvents.<sup>3–6</sup> From the viewpoint of magnetism, it would be interesting to produce organic/inorganic hybrids between such long-chain organic molecules with structural flexibility and layered copper hydroxides, because the materials,  $\text{Cu}_2(\text{OH})_3\text{X}$  (X = intercalated anion, such as  $\text{NO}_3^-$ , alkane carboxylates, etc.), show a magnetic variety which drastically depends on the molecular shape and alignment of X.<sup>7,8</sup> The origin of the magnetic variety is thought to be the sensitivity of the magnetic interactions to the Cu–OH–Cu bridging angles in the  $[\text{Cu}_2(\text{OH})_3]^-$  network.<sup>9</sup> If the magnetic properties of the inorganic layer are affected by a structural modification in the organic layer which is introduced by a stimulus to it, then the hybrid can be regarded as a controllable and/or switchable magnetic material, in which the inorganic layer carries magnetic moments and the organic layer plays a role of an organizer of the magnetic properties of the inorganic layers. In this work, we intercalated an organic anion, 8-((*p*-phenylazo)phenyl)oxy)octanoate, into the  $[\text{Cu}_2(\text{OH})_3]^-$  interlayer and investigated the magnetic properties of the intercalation compound. We report a reversible phase transition which takes place in two organic solvents and results in a drastic change of the magnetic properties.

The starting compound, copper hydroxy acetate,<sup>10</sup> and the sodium salt of the guest anion, 8-((*p*-phenylazo)phenyl)oxy)octanoate,<sup>11</sup> were prepared by literature methods. The organic/inorganic hybrid,  $\text{Cu}_2(\text{OH})_3[8-((p\text{-phenylazo)phenyl)oxy)octanoate]$ , was obtained by anion exchange: 200 mg of the parent copper hydroxide compound and 1 g of the sodium carboxylate were dispersed in 50 mL of methanol. The mixture was stirred for a day at 50 °C, and the obtained material was filtrated, washed with methanol, and dried under vacuum. (Anal. Calcd (found) for the organic/inorganic hybrid,  $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_6\text{Cu}_2$ : C, 46.43 (47.42); H, 5.06 (5.33); N, 5.42 (5.65).) The agreement between the calculation and observation indicates completeness of the anion exchange.

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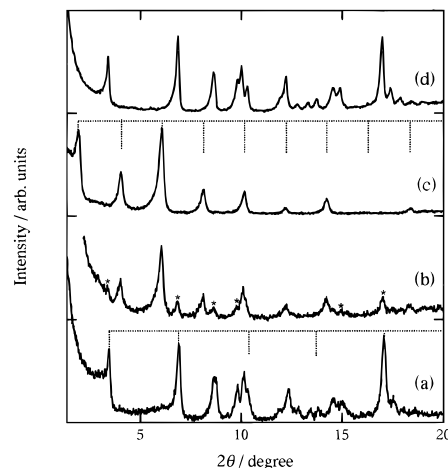
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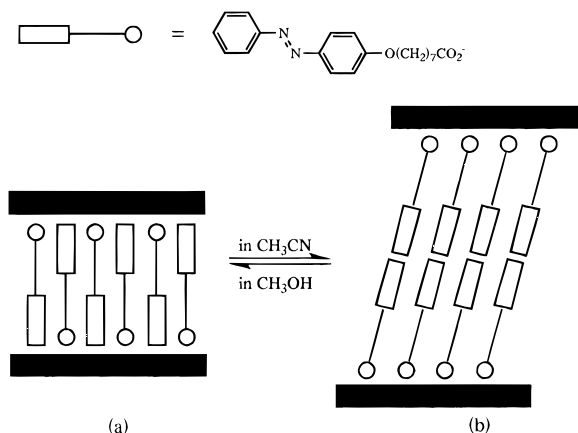
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**Figure 1.** Cu K $\alpha$  X-ray diffraction patterns of  $\text{Cu}_2(\text{OH})_3[8-((p\text{-phenylazo)phenyl)oxy)octanoate]$  obtained by soaking in acetonitrile for 0 h (a), 24 h (b), and 48 h (c) and in hot methanol for 24 h (d). For details, see the text.



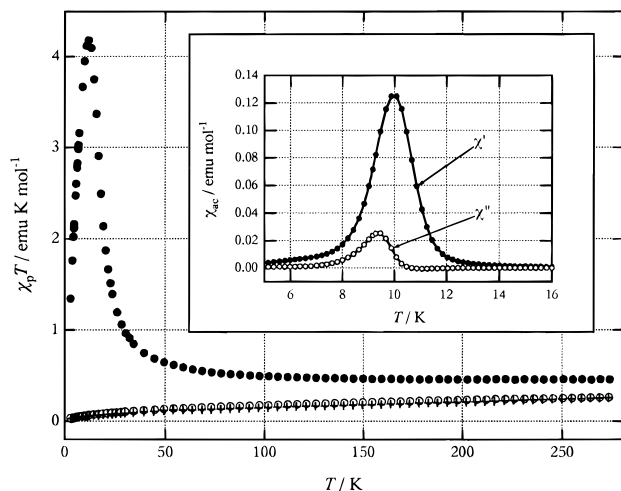
**Figure 2.** Schematic presentation of the packing change of the organic layer in methanol (a) and acetonitrile (b).

The powder X-ray diffraction pattern of the parent compound,  $\text{Cu}_2(\text{OH})_3\text{CH}_3\text{COO}\cdot\text{H}_2\text{O}$ , is reported in ref 12. The basal spacing is 9.3 Å before the anion exchange. Figure 1a shows the diffraction pattern of the obtained hybrid, which was taken on a Rigaku X-ray powder diffractometer (RAD3C) using Cu K $\alpha$  radiation. There is a series of (00 $l$ ) reflections with an equivalent interval, indicating a layered structure in it. The interlayer distance was estimated to be 20.7 Å, subtracting the calculated thickness of the inorganic host layer from the basal spacing of 25.5 Å obtained from the periodicity in the pattern. It corresponds well to the calculated anion height of 21.7 Å.<sup>13</sup> This means an interdigitated monolayer structure of the organic layer, as schematically shown in Figure 2a.

The organic layer of the material was found to show a drastic structural change in acetonitrile. Although the organic/inorganic hybrid was insoluble to the solvent, we dispersed the sample in it and stirred the mixture for 2 days. Figure 1b,c represents the X-ray diffraction patterns of the material after the soaking for 24 and 48 h, respectively. The measurements were carried out, after the samples were dried in vacuum. The peaks of the original hybrid remarkably decrease in intensity after 24 h (starred in Figure 1b) and completely disappear after 48 h. Instead of them, new (00 $l$ ) reflections appear and intensify gradually. The peak interval indicates that the interlayer

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**Figure 3.** Temperature dependence of the paramagnetic susceptibilities  $\chi_p$  of the original (○) and revived (+) monolayer phases and of the bilayer phase (●). The inset shows temperature dependence of the ac susceptibilities  $\chi_{ac}$  of the bilayer phase; real (●) and imaginary (○) parts.

distance of the transformed hybrid in acetonitrile is 38.7 Å, which is almost twice as long as the molecular height of the anion. After soaking, the organic anion is considered to form a membrane-like bilayer, as shown in Figure 2b. The results of the elemental analyses of the bilayer phase (found: C, 47.26; H, 5.13; N, 5.68) agree with those of the original monolayer phase, indicating that there is no acetonitrile remaining in the bilayer phase. The phenomenon is hardly regarded as a simple swelling, although the organic solvent must play an important role in the transformation of the organic layer.

Furthermore, the bilayer hybrid reverts into the monolayer structure in hot methanol. Figure 1d shows the powder X-ray pattern of the hybrid which was obtained by soaking the bilayer hybrid in methanol at 50 °C for 24 h. It agrees with that of the original monolayer hybrid, shown in Figure 1a. The monolayer transformation reversibly takes place in the two solvents.

The dc magnetic susceptibilities of the monolayer and bilayer phases were examined on a Faraday balance<sup>14</sup> in the range of 3–280 K under the field of 1 T. The paramagnetic susceptibility,  $\chi_p$ , was obtained from the dc susceptibility, subtracting the Pascal diamagnetic susceptibility of  $-1.58 \times 10^{-4}$  emu mol<sup>-1</sup>, where one-half of Cu<sub>2</sub>(OH)<sub>3</sub>X was adopted as the molar unit. We did not compensate the effect of nonlinear relation between the magnetization and the applied field, observed at low temperatures, in the calculation of the dc susceptibility. The open circles in Figure 3 show the temperature dependence of  $\chi_p T$  of the original monolayer phase. The value of  $\chi_p T$  gradually decreases with decreasing temperature down to 3 K, meaning a dominance of an antiferromagnetic interaction. Above 150 K, the behavior can be well explained in terms of the Curie–

Weiss law with the Curie constant of 0.40 emu K mol<sup>-1</sup> and the Weiss constant of –159 K.

The closed circles in Figure 3 show the temperature dependence of  $\chi_p T$  of the bilayer phase obtained in acetonitrile. It shows a big anomaly below 50 K, compared with the monotonical temperature dependence of the original monolayer phase. The inset of Figure 3 shows the temperature dependence of the ac susceptibilities, which were measured on a Lake Shore ac susceptometer (ACS 7000) in an alternating field of 5 Oe (125 Hz). In this inset, the circles and squares indicate the real ( $\chi'$ ) and imaginary ( $\chi''$ ) parts, respectively. The plots of  $\chi'$  make an anomalous peak around 10 K whose maximum value is 0.13 emu mol<sup>-1</sup>.  $\chi''$  also shows an anomaly at 10.8 K, after temperature independent behavior above it. The divergence of the ac susceptibility indicates a ferromagnetic order at  $T_c = 10.8$  K. The magnetization curve at 4.5 K shows typical behavior of a weak ferromagnet; an abrupt increase at the lower fields, followed by a gradual increase without showing saturation at the higher fields (not shown). The residual magnetization is 1460 erg Oe<sup>-1</sup> mol<sup>-1</sup> which corresponds to a canting angle of 13.6° between two moments. The behavior is very similar to those of Cu<sub>2</sub>(OH)<sub>3</sub>(*n*-C<sub>*m*</sub>H<sub>2*m*+1</sub>COO) (*m* = 7, 8, and 9), although their  $T_c$  are ca. 20 K.<sup>7,8</sup>

The crosses in Figure 3 show the temperature dependence of  $\chi_p T$  of the monolayer phase revived by soaking the bilayer phase in hot methanol. The magnetic behavior is identical with that of the original hybrid, which supports the reversible transformation.

We found the reversible monolayer phase transition of the organic layer in the organic/inorganic hybrid, Cu<sub>2</sub>(OH)<sub>3</sub>[8-(*p*-(phenylazo)phenyl)oxy]octanoate], which is activated by soaking in acetonitrile and hot methanol. Such a reversible monolayer transition is quite unusual in organic/inorganic hybrid layered materials. In addition the interesting transformation of the organic layer results in the drastic change of the magnetic properties of the inorganic layer. While the monolayer phase is paramagnetic down to 3 K, the bilayer phase becomes the weak ferromagnet with  $T_c = 10.8$  K. The organic layer changes the structure according to the atmospheres of the organic solvents. The structural change in the organic layer affects the structure of the inorganic layer and modifies the physical properties in it. The story suggests the possibility of switchable and/or controllable physical properties, derived from cooperation between an inorganic host carrying a source of physical properties, such as magnetism, conductivity, etc., and an organic guest playing a role of sensor.

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