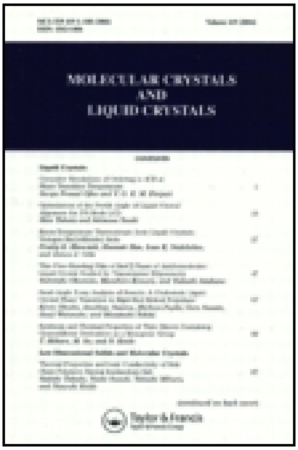

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Solvent-Mediated Magnetic Change in Copper-Hydroxy Intercalation Compounds

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A reversible structural transformation of the basic copper hydroxides $Cu_2(OH)_3$[8-((*p*-(phenylazo)phenyl)oxy)octanoate] occurs as a result of soaking in hot methanol and acetonitrile. X-ray diffraction patterns indicate that the organic layer in the material exhibits an interdigitated monolayer structure in hot methanol, while it does a membrane-like bilayer structure in acetonitrile. The monolayer phase is paramagnetic down to 3 K, while the bilayer phase shows a weak ferromagnetism below 10.8 K. The reversible packing change of the organic guest molecule is accompanied by drastic modification in the magnetic properties of the inorganic layer.

Keywords: layered copper hydroxides; intercalation; organic solvent; phase transition; magnetic properties

INTRODUCTION

Layered copper hydroxides, $Cu_2(OH)_3X$ (X = inorganic anion, carboxylate and so on), attract interest as two-dimensional magnetic material.[1,2] Figure 1 shows the crystal structure of copper hydroxy nitrate ($X = NO_3$).[3,4] The structure of the copper hydroxy layer is similar to that of the $Cd(OH)_2$ layer: the structure of the former can be obtained by replacing one fourth of the OH in $Cd(OH)_2$ with the guest anion X periodically. The anion X is located between the inorganic layers and can be exchanged with other organic anions, so that various organic-inorganic nanocomposite hybrids can be easily produced.[5] The copper hydroxy layer shows a magnetic variety which depends drastically on the molecular shape and orientation of X.[6-8] The

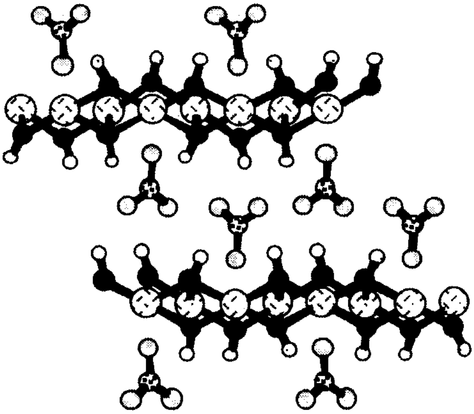
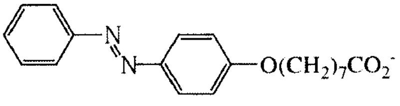


Figure 1 Crystal structure of $Cu_2(OH)_3X$ ($X = NO_3$).

origin of the magnetic variety is due to the sensitivity of the nearest-neighbor Cu-Cu magnetic interactions to the Cu-O-Cu bridging angles in the $[Cu_2(OH)_3]^+$ network.[9] We envisage that the magnetic properties of the copper hydroxy layer are affected by a structural phase transition in the guest assemble layer which is introduced to it by a stimulus. Such a compound can be regarded as a controllable and/or switchable magnetic material, in which the inorganic layer carries magnetic moments and the organic layer plays the role of organizer to the magnetic properties of the inorganic layers.

In this work, we intercalated an organic anion, 8-((*p*-(phenylazo)-phenyl)oxy)octanoate (Scheme I), into the $[Cu_2(OH)_3]^+$ 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.



Scheme I

EXPERIMENTALS

The parent compound (X = $CH_3COO \bullet H_2O$)[5] and the guest anion, 8-((*p*-(phenylazo) phenyl)oxy)octanoate,[10] were obtained by the literature methods. The intercalation of the guest anion was performed by means of the ion-exchange; 200 mg of the parent compound and 1 g of the sodium salt of the guest anion were dispersed in 50 ml of methanol. The mixture was stirred for a day at 50 °C, and the obtained intercalation compound was filtrated, washed with methanol, and dried under vacuum. Anal. Calcd (found) for the intercalation compound, $C_{20}H_{26}N_2O_6Cu_2$: 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.

The X-ray diffraction data were taken on a Rigaku X-ray powder diffractometer (RAD3C) using Cu-Kα radiation. The dc magnetic susceptibilities of the intercalation compounds were examined on a Faraday balance[11] in the 3-280 K range under the field of 1 T. The paramagnetic susceptibility, χ_p, was obtained from the dc susceptibility, by subtracting the Pascal diamagnetic susceptibility of -1.58×10^{-4} emu mol^{-1}, for a half of the $Cu_2(OH)_3X$. The ac susceptibilities were measured on a Lake Shore ac susceptometer (ACS 7000) in an alternating field of 5 Oe (125 Hz).

RESULTS AND DISCUSSION

The powder X-ray diffraction pattern of the parent compound, $Cu_2(OH)_3CH_3COO \cdot H_2O$, is reported in ref. 12. The basal spacing is 9.3 Å before the anion exchange. Figure 2(a) shows the diffraction pattern of the obtained intercalation compound. 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. This corresponds to the calculated anion height of 21.7 Å.[13] These results indicate an interdigitated monolayer structure of the organic layer, as schematically shown in Fig. 3(a).

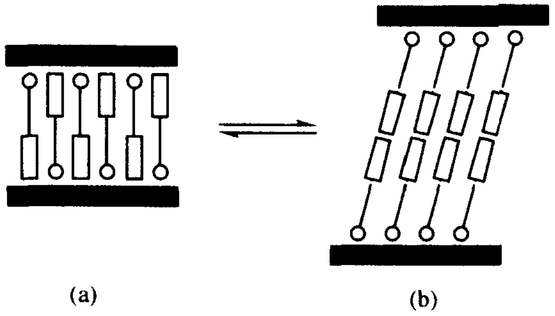


Figure 3 Schematic presentation of the packing change of the organic layer in methanol (a) and acetonitrile (b).

phase in acetonitrile is 38.7 Å, which is almost twice as long as the molecular height of the anion. After the soaking, the organic anions are considered to form a membrane-like bilayer, as shown in Fig. 3(b). The results of the element 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 phase reverts into the monolayer structure in hot methanol. Figure 2(d) shows the powder X-ray pattern of the intercalation compound which was obtained by soaking the bilayer phase in methanol at 50 °C for 24 hrs. It agrees with that of the original monolayer phase, shown in Fig. 3(a). The mono-bilayer transformation reversibly takes place in the two solvents.

The mono-bilayer transformation observed in our experiment is similar to soluto-induced interdigitations in phospholipid assembles. Phospholipid molecules, which are major lipid components of biomembranes, assemble spontaneously in aqueous environments, usually forming a bilayer structure. It is known that a number of lipids form an interdigitated monolayer in the presence of alcohols.[14] The induction of interdigitation is dependent upon alcohol concentration, lipid chain length and temperature. Since the van der Waals energy of interaction in the closely-packed

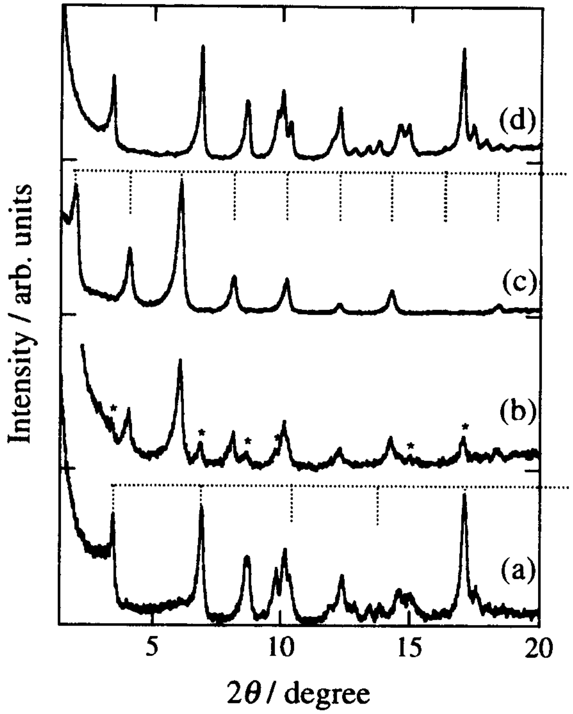


Figure 2 Cu-Kα X-ray diffraction patterns of $Cu_2(OH)_3[8\text{-}((p\text{-}(phenylazo)phenyl)oxy)octanoate]$ obtained by soaking in acetonitrile for 0 hr (a), 24 hrs (b) and 48 hrs (c), and by soaking in hot methanol for 24 hrs (d).

The organic assembly of the material was found to show a drastic structural change in acetonitrile. Although the intercalation compound was insoluble to the solvent, we dispersed the original phase in it and stirred the mixture for two days. Figures 2(b) and (c) show the X-ray diffraction patterns of the intercalation compound after being soaked for 24 and 48 hours respectively. The measurements were carried out after the samples were dried in vacuum. The peaks of the original phase remarkably decrease in intensity after 24 hours (starred in Fig. 2(b)) and completely disappear after 48 hours. Instead of them, new (00*l*) reflections appear and intensify gradually. The peak interval indicates that the interlayer distance of the new

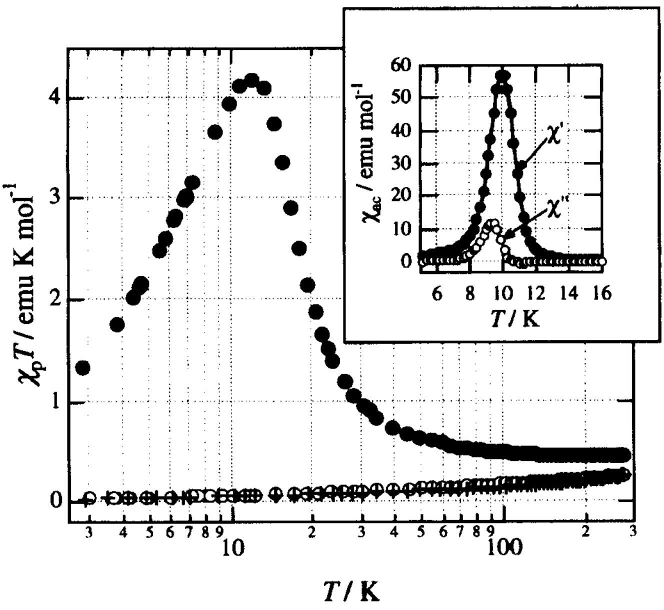


Figure 4 Temperature dependence of the paramagnetic susceptibilities of the original (○) and revived (+) monolayer phases and of the bilayer phase (●). The inset shows the temperature dependence of the ac susceptibilities of the bilayer phase; real (●) and imaginary (○) parts.

interdigitated monolayer form is greater than that in the bilayer one, this commonly favors the formation of the former structure.[16] This interaction is counterbalanced by the repulsive interaction of the terminal hydrophobic group of the phospholipid molecule with the aqueous phase as they are exposed to the polar environment at the interface. When alcohol is added into the system, the phase transformation to the interdigitated form occurs. This takes place because the alcohol molecules cover the hydrophobic terminal and reduce the repulsive interaction. The soluto-induced behaviors found in this work may also occur by the similar mechanism.

The open circles in Fig. 4 represent the temperature dependence of χ_pT of the original monolayer phase. The value of χ_p T gradually decreases with decreasing temperature down to 3 K, indicating 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^{-1} and the Weiss constant of -159 K. The closed circles in Fig. 3 show the temperature dependence of χ_pT of the bilayer phase obtained in acetonitrile. A major anomaly is shown below 50 K, compared with the monotonical temperature dependence of the original monolayer phase. The inset of Fig. 4 shows the temperature dependence of the ac susceptibilities of the bilayer phase. In this inset, the circles and squares indicate the real (χ') and imaginary (χ'') parts, respectively. The plots of χ' make an anomalous peak around 10 K, whose maximum value is 57 emu mol^{-1}. χ'' 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^{-1} mol^{-1}, which corresponds to a canting angle of 13.6° between two moments. This behavior is very similar to those of $Cu_2(OH)_3(n\text{-}C_mH_{2m+1}COO)$ (m = 7, 8 and 9), though their T_c are ca. 20 K.[6,7] The crosses in Fig. 4 represent the temperature dependence of χ_pT of the monolayer phase revived by soaking the bilayer phase in hot methanol. The magnetic behavior is identical to that of the original phase, which supports the reversible transformation.

CONCLUSION

We found the reversible mono-bilayer phase transition of the organic layer in the intercalation compound, $Cu_2(OH)_3$[8-((p-(phenylazo) phenyl)oxy)-octanoate], which is activated by soaking in acetonitrile and hot methanol. Such a reversible mono-bilayer transition is quite unusual in organic-inorganic hybrid layered materials. In addition, the interesting transformation of the organic assemble results in drastic changes in 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 assembly changes the structure, according to the atmospheres of the organic solvents. The structural change in the organic assemble affects the structure of the inorganic layer and modifies the physical properties in it. This study 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 the role of sensor.

Acknowledgments
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