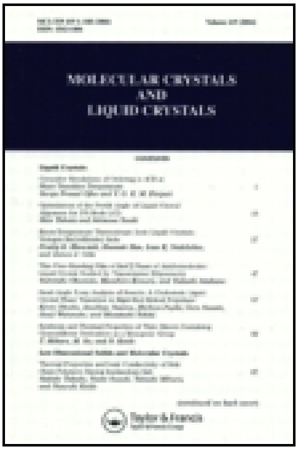


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photoisomerism of Azobenzene Derivatives in Layered Magnetic Materials

Wataru Fujita [a] & Kunio Awaga [a]

[a] Department of Basic Science, The University of Tokyo, Komaba, Meguro, Tokyo, 153, Japan

Version of record first published: 04 Oct 2006

To cite this article: Wataru Fujita & Kunio Awaga (1998): Photoisomerism of Azobenzene Derivatives in Layered Magnetic Materials, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 315:1, 29-34

To link to this article: http://dx.doi.org/10.1080/10587259808044306

Mol. Cryst. Liq. Cryst., 1998, Vol. 315, pp. 29–34
Reprints available directly from the publisher
Photocopying permitted by license only

Photoisomerism of Azobenzene Derivatives in Layered Magnetic Materials

WATARU FUJITA and KUNIO AWAGA*
Department of Basic Science, The University of Tokyo, Komaba, Meguro,
Tokyo 153, Japan

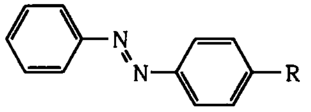
The copper hydroxy layered hybrids, $Cu_2(OH)_3X$, where X = *p*-(phenylazo)-benzoate **1** and X = 8-((*p*-(phenylazo)phenyl)oxy)octanoate **2**, were prepared. The material **1** is paramagnetic with an antiferromagnetic interaction above 3 K, while **2** becomes a weak ferromagnet below ca. 10 K. In **2** the *trans-to-cis* isomerization reaction of the interlayer azobenzene moiety takes place by UV-light illumination, although the photoreaction is irreversible. There is little change in the magnetic properties, caused by the photoreaction.

Keywords: Layered Copper Hydroxides, Intercalation, Azobenzenes, Magnetic Properties, Photoisomerism

INTRODUCTION

Basic copper hydroxides, $Cu_2(OH)_3X$ (X=NO_3, carboxylate and so on), attract much interest as a two-dimensional magnetic material because of its lamellar structure. The counter anion X is located in the interlayer, and coordinates to the copper ion. It is known that the anion is exchangeable with various organic anions and various intercalation compounds can be easily produced.[1] We have found that the copper hydroxy layer shows a magnetic variety which drastically depends on the molecular shape and alignment of X.[2] 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 $[Cu_2(OH)_3]^-$ network.[3]

In this study, we have intercalated the azobenzene derivatives (Scheme I), into the copper hydroxides interlayers and have investigated the magnetic properties of the layered hybrids and the photoisomerism of the azobenzene moiety in the interlayer.



$R = CO_2^-$
$= O(CH_2)_7CO_2^-$

Scheme I

MATERIALS

The parent compound, $Cu_2(OH)_3CH_3CO_2{\bullet}H_2O$,[1] and the photochromic anions, *p*-(phenylazo)benzoate[4] and 8-((*p*-(phenylazo)phenyl)oxy)octanoate,[5] were obtained by the literature methods. The layered hybrid, $Cu_2(OH)_3$[*p*-(phenylazo)benzoate] **1**, was prepared by dispersing microcrystalline powder of the parent compound in aqueous solution of *p*-(phenylazo)benzoate for a day at room temperature. $Cu_2(OH)_3$[8-((*p*-(phenylazo)phenyl)oxy)octanoate] **2** was prepared by the method of ref. 6. Anal. Calcd (found) for **1**, $C_{13}H_{12}N_2O_5Cu_2$: C, 38.72 (39.45); H, 2.98 (3.61); N, 6.94 (6.73), and **2**, $C_{20}H_{28}N_2O_6Cu_2$: C, 46.43 (47.42); H, 5.03 (5.33); N, 5.42 (5.65). The results of the elemental analyses indicate completeness of the ion-exchanges.

RESULTS AND DISCUSSION

X-ray diffraction patterns

Figures 1(a) and 1(b) show the Cu Kα X-ray powder diffraction patterns of the layered hybrids **1** and **2**, respectively. The materials show intense (00*l*) reflections, indicating the layered structure in them. The interlayer distance was estimated by subtracting the thickness (4.8 Å) of the inorganic host layer from the distance between two neighboring planes of class (00*l*). The intercalations of the azobenzene derivatives increase the interlayer distance of the parent compound (4.5 Å). The interlayer distance of **1** is 14.6 Å, which is almost equal to the anion height of 12.0 Å. The anion is thought to form an interdigitated monolayer structure. The interlayer distance of **2** is 38.7 Å, which is almost double of the corresponding anion height of 21.7 Å, and suggests a membrane-like bilayer structure.

Magnetic Properties

The temperature dependences of the magnetic susceptibilities of **1** and **2** were

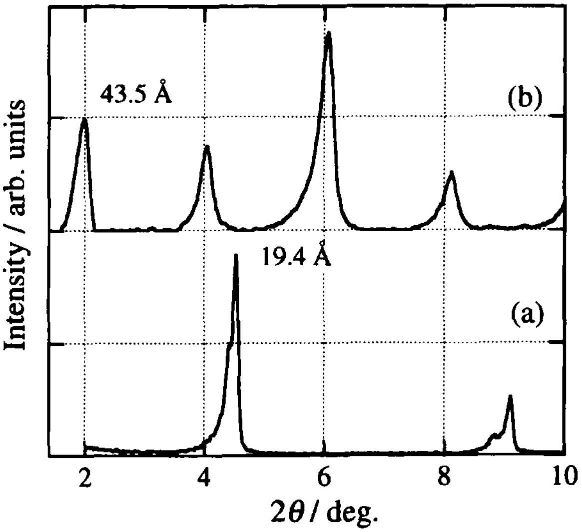


FIGURE 1 Cu Kα X-ray diffraction patterns of the layered hybrids **1** (a) and **2** (b).

examined in the range 3-280 K under the field of 1 T on a Faraday balance.[7] We adopt a half of $Cu_2(OH)_3X$ as the molar unit. The opened circles in Fig. 2, where the x axis is in a log scale, show the result on **1**. The value of χ_p gradually increases with decreasing temperature down to 3 K. The behavior above 100 K is well fitted to the Curie-Weiss law with the Curie constant C of 0.429 emu K $mol(Cu)^{-1}$ and the Weiss constant θ of -83 K. No magnetic phase transition in **1** is observed above 3 K. The open squares in Fig. 2 show the χ_p value of **2**. The dependence obeys the Curie-Weiss law above 150 K with C = 0.461 emu K $mol(Cu)^{-1}$ and $\theta = 1.5$ K. However χ_p shows an abrupt increase below 50 K and almost saturates below 10 K. The ac susceptibilities of **2** indicate a ferromagnetic transition at 10.8 K (not shown). The inset of Fig. 2 shows the magnetization curve of **2** measured with increasing field at T = 4.5 K. The magnetization of the sample shows a gradual increase at the higher fields, in contrast to the abrupt jump at the lower fields. This is typical of a weak ferromagnet. The residual magnetization of **2** is 1488 emu Oe^{-1} $mol(Cu)^{-1}$, which corresponds to the canting angle of 13.6°.

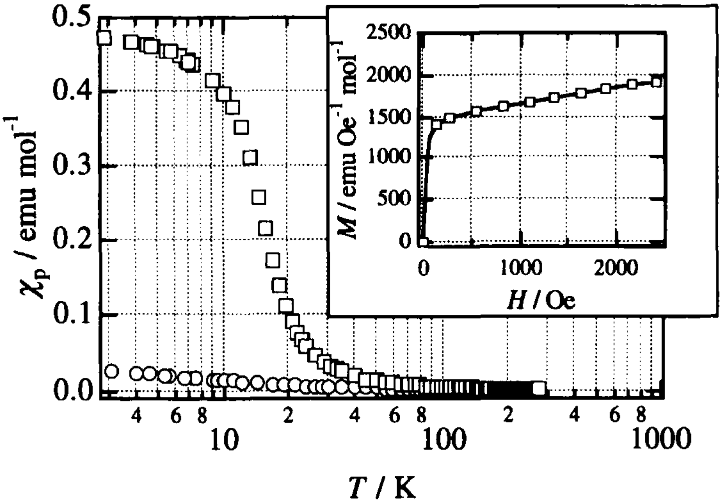


FIGURE 2 Temperature dependence of the paramagnetic susceptibilities χ_p of the layered hybrids **1** (circles) and **2** (squares). The inset shows the magnetization curve of **2** at 4.5 K.

Photoisomerism of Azobenzene Moiety

The absorption spectra of the powder samples of the hybrids, **1** and **2**, were examined before and after the photoirradiation of UV-light (300-400 nm), in order to see the *trans-cis* transformation of the azobenzene moiety. We measured the relative diffuse transmittance of a KBr-diluted pellet of the sample, using an Ulbricht sphere. The obtained transmittance was converted into the absorbance by the Kubelka-Munk equation. The results are shown in Fig. 3, where the solid lines show the absorption spectra of the hybrids before the irradiation and the broken lines do those after it. The spectrum in Fig. 3(a) is that of the parent compound, $Cu_2(OH)_3(CH_3COO){\bullet}H_2O$, which shows the absorption of the copper hydroxides layer. The compound is transparent in the range $\lambda >$ ca. 300 nm. Figure 3(b) shows the spectra of **1**. There is little change caused by the irradiation. The band at 315 nm is assigned to the characteristic π-π^* transition in the *trans*-azobenzene moiety. The results on **2** are shown in Fig. 3(c). The π-π^* transition at 350 nm appearing before the irradiation, decreases in intensity after it. The *trans*-isomer is converted into

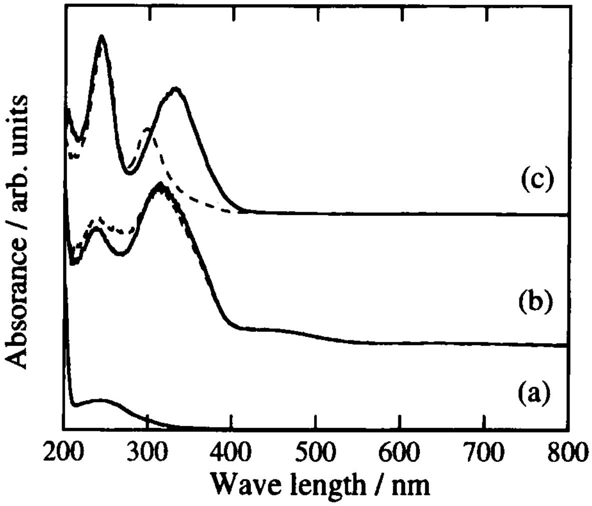


FIGURE 3 Absorption spectra of the parent compound (a), the layered hybrids **1** (b) and **2** (c); solid lines show that before irradiation and broken lines that after irradiation.

the *cis*-one in **2**, although there is no photoisomerization in **1**. It is worth noting here that the *cis-to-trans* isomerization reaction in **2** does not occur by the irradiation of $\lambda > 400$ nm. The reaction is irreversible.

We calculated the packing coefficient of the hybrids, using the results of the powder X-ray analyses and the structural parameters of $Cu_2(OH)_3NO_3$.[8] There is a big difference in the value between **1** and **2**. The packing coefficient of **1** is 0.62, which corresponds to those of the molecular crystals. Under such dense packing, the *trans-to-cis* isomerization would hardly take place, because it is associated with a large structural change.[9] On the other hand, the structural change is not suppressed by steric hindrance in **2**, because the packing coefficient of **2** is 0.39. The interlayer of **2** allows the guest molecule to show the isomerization reaction.

We carried out magnetic measurements on both the *trans* and *cis*-isomers of **2**. However there was no magnetic difference between them. Unfortunately, the photochemical reaction is not linked to the magnetic system. This could be related to the fact that the azobenzene part is dislodged from the inorganic layer with the alkyl chains.

CONCLUSION

We intercalated the azobenzene derivatives into the copper hydroxides layers. It is suggested that the guest anions form interdigitated monolayer and bilayer structures in **1** and **2**, respectively. **1** shows the paramagnetic behavior above 3 K, while **2** is a weak ferromagnet below ca. 10 K. We observed the *trans-to-cis* isomerization reaction of the azobenzene moiety in **2** by the photoirradiation. However, the photoreaction is irreversible and there is little magnetic change.

We are now working on intercalation of various photochromic anions into layered magnetic materials, in order to get a coupling between the photochemical reaction and the magnetism.

Acknowledgment

We thank Prof. Katsuhiko Takagi of Nagoya University for helpful discussion on photochemical reactions in intercalation compounds. This work was supported by the Grant-in-aid for Scientific Research from the Ministry of Education, Science, and Culture, Japanese government and CREST of the Japan Science and Technology Corp.(JST).

References

[1.] S. Yamanaka, T. Sako and M. Hattori, *Chem. Lett.*, 1869 (1989).

[2.] W. Fujita and K. Awaga, *Inorg. Chem.*, **35**, 1915 (1996); P. Rabu, S. Rouba, V. Laget, C. Hornick and M. Drillon, *J. Chem. Soc. Chem. Commun.*, 1107 (1996).

[3.] W. Fujita, K. Awaga and T. Yokoyama, *Inorg. Chem.*, **36**, 196 (1997).

[4.] E. C. Horning, *Org. Syn.*, *Coll. Vol. III* , John Wiley & Sons, Inc., New York, p.711 (1965).

[5.] M. Shimomura, R. Ando and T. Kunitake, *Ber. Bunsenges. Phys. Chem.*, **87**, 1134 (1983).

[6.] W. Fujita and K. Awaga, *J. Am. Chem. Soc.*, **119**, 4563 (1997).

[7.] K. Awaga and Y. Maruyama, *Chem. Mater.*, **2**, 535 (1990).

[8.] H. Effenberger, *Z. Krist.* **165**, 127 (1983).

[9.] K. Takagi, T. Shichi, H. Usami and Y. Sawaki, *J. Am. Chem. Soc.*, **115**, 4339 (1993).