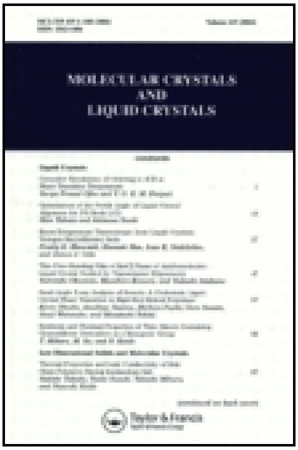

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Magnetic Properties Of Basic Copper(?) Formates

Kenji Ueda [a], Satoshi Takamizawa [a], Wasuke Mori [a] & Kizashi Yamaguchi [a]

[a] Department of Chemistry, Faculty of science, Osaka University, Toyonaka, Osaka, 560, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Kenji Ueda, Satoshi Takamizawa, Wasuke Mori & Kizashi Yamaguchi (1996): Magnetic Properties Of Basic Copper(?) Formates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 286:1, 17-22

To link to this article: http://dx.doi.org/10.1080/10587259608042259

Mol. Cryst. Liq. Cryst., 1996, Vol. 286, pp. 17–22
Reprints available directly from the publisher
Photocopying permitted by license only

MAGNETIC PROPERTIES OF BASIC COPPER(II) FORMATES

KENJI UEDA, SATOSHI TAKAMIZAWA, WASUKE MORI AND KIZASHI YAMAGUCHI
Department of Chemistry, Faculty of science, Osaka University, Toyonaka, Osaka 560, Japan

Abstract Cu(HCOO)(OH) exhibits a strong ferromagnetic interaction (θ =+43K). The susceptibility shows a sharp maximum at T_m=21K and a plateau below 12K. This magnetic behavior is characteristic of antiferromagnetic materials. The spin-flop behavior is observed below T_m. To examine the spin-flop behavior of Cu(HCOO)(OH), magnetic phase diagram was drawn up. Magnetic phase diagram of Cu(DCOO)(OD) was also constructed to examine whether magnetic interaction between layers is due to hydrogen bond or not. Between them there is little difference in the phase diagram, but there is a remarkable difference in the hysteresis curves at 2K. Besides, temperature dependence of susceptibility and hysteresis curve at 1.8K of $Cu_3(HCOO)_2(OH)_4$ was measured. In consequence it was found that this material also showed spin-flop behavior.

INTRODUCTION

There are far more types of copper(II) formates than of other copper(II) carbonates and they have various structures. For example, three isomers can be found for anhydrous copper(II) formates. Numerous ways of bridges between Cu(II) ions in these compounds can be seen, producing various types of magnetic interactions. Therefore copper(II) formates are suitable for examining the relation between the molecular structure and the magnetic behavior, and new types of copper(II) formates, if they can be prepared, are expected to show unique magnetic properties.

From this point of view, magnetic properties of basic copper(II) formates has been studied in detail [1,2]. It has been found so far that Cu(HCOO)(OH) exhibited characteristic behaviors of spin-flop phenomenon [1], but more detailed examination is strongly needed. In this study the spin-flop behavior of Cu(HCOO)(OH) was clarified by performing various magnetic measurements and constructing magnetic phase diagram of this material.

The magnetic properties of the other basic copper(II) formate, $Cu_3(HCOO)_2(OH)_4$, were also investigated.

EXPERIMENTAL

Crystals of Cu(HCOO)(OH) and $Cu_3(HCOO)_2(OH)_4$ were prepared by previously reported procedures [1]. All magnetic measurements were performed by using a SQUID magnetometer (quantum design MPMS-5S). The following values were used: Cu^{2+}(-11), OH^-(-12), and $HCOO^-$ (-20) for diamagnetic corrections (10^{-6} emu mol^{-1}) [3] and 60×10^{-6} emu mol^{-1} for temperature independent paramagnetism .

Crystal structure of Cu(HCOO)(OH) is illustrated in Fig. 1 [2]. The HCOO and OH group bridge the neighboring copper ions and infinite zigzag chains are formed along b axis. The chains are connected together by the bonds between copper

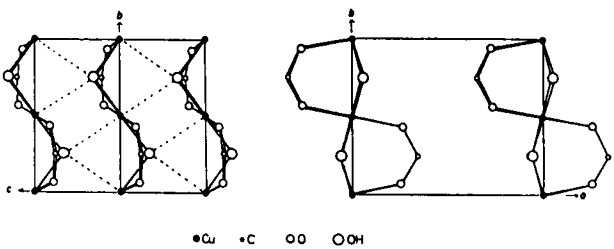

FIGURE 1 Crystal structure of Cu(HCOO)(OH).

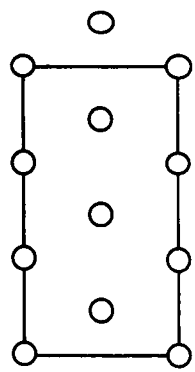

FIGURE 2 Positions of Cu(II) ions in $Cu_3(HCOO)_2(OH)_4$.

ions and hydroxy groups, and the layers are formed so that the spins interact ferromagnetically. There are no shorter contacts than 4.3 Å between the layers except for hydrogen bond. The magnetic transition may take place by the antiferromagnetic interaction between the layers.

As for $Cu_3(HCOO)_2(OH)_4$, the cell constants and positions of copper ions (Fig. 2) were defined by Weissenberg photographs.

RESULTS AND DISCUSSION

Cu(HCOO)(OH)

Hysteresis and magnetization curves at various temperatures of this compound are shown in Fig. 3. In the magnetic field region lower than 1T, irregularity indicating spin-flop phenomenon is observed in the magnetization curves at 2-20K, but it was not observed at 25K. And peculiar hysteresis is observed in the field range of ± 2T-±3T in the hysteresis curve at 2K.

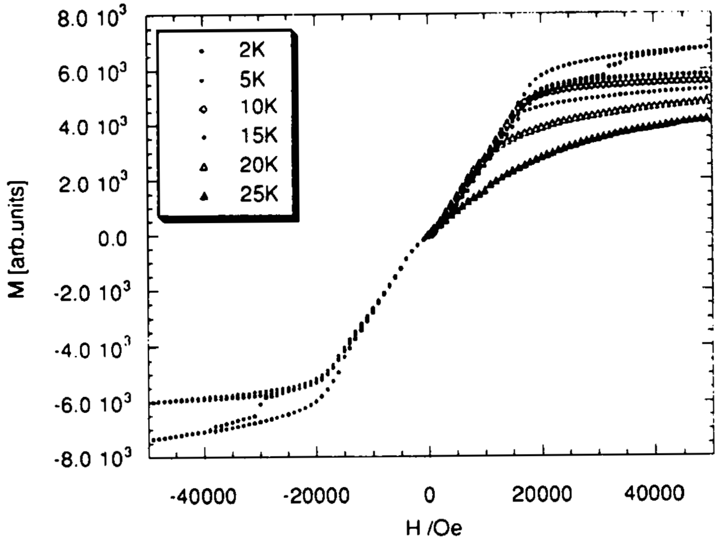

FIGURE 3 Hysteresis curves of Cu(HCOO)(OH).

The Xa-T curves of Cu(HCOO)(OH) in various fields, which are shown in Fig. 4, indicate the field dependence. As the magnetic field increases, the peak at T_m becomes more dull and is shifted to lower temperature, vanishing finally at 1.4T.

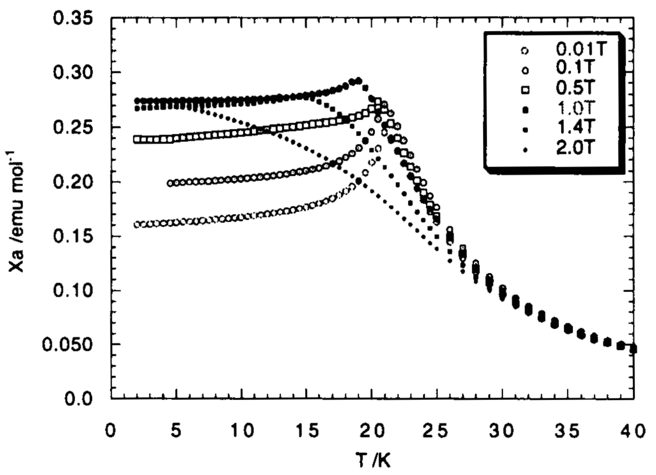

FIGURE 4 Temperature dependence of susceptibilities of Cu(HCOO)(OH) in various fields.

Magnetic phase diagram (Fig. 5) of Cu(HCOO)(OH), constructed from these measurements consists of antiferromagnetic phase (AF), spin-flop phase (SF) and paramagnetic phase (P), where Hsf and Hc denote spin-flop field and critical field, respectively. There is a triple point at field 0.3T and temperature 21K. The magnetic phase diagram of Cu(DCOO)(OD) is shown in Fig. 6.

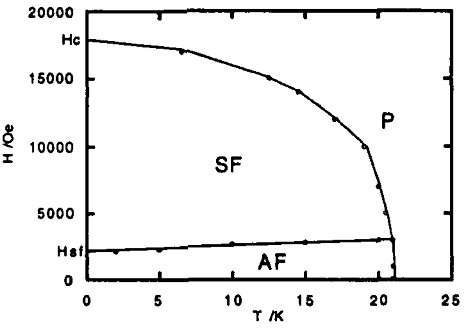

FIGURE 5 Magnetic phase diagram of Cu(HCOO)(OH).

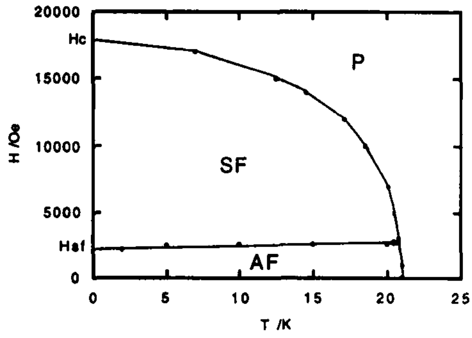

FIGURE 6 Magnetic phase diagram of Cu(DCOO)(OD).

There is little difference between diagrams of Cu(HCOO)(OH) and of Cu(DCOO)(OD), and a triple point of the latter also exists at the same point as Cu(HCOO)(OH). However, a remarkable difference is observed in hysteresis curve at 2K (Fig. 7). As values of spin-flop field and critical field are almost the same for two complexes, the differences between them may be summarized in the next two points. First, peculiar hysteresis exists in the curve of Cu(HCOO)(OH). Second, the saturation is not complete at 5T.

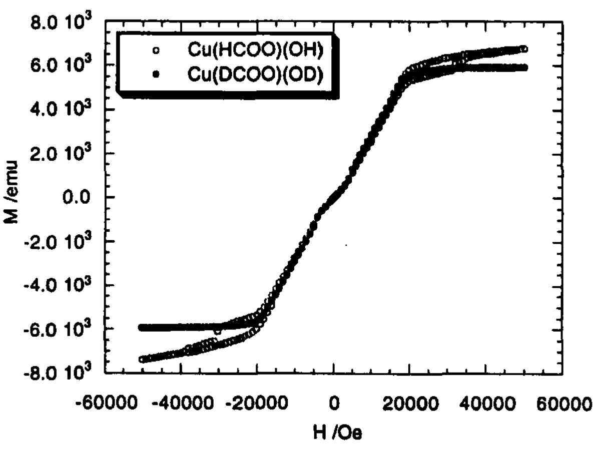

FIGURE 7 Hysteresis curves at 2K of Cu(HCOO)(OH) and Cu(DCOO)(OD).

The following ideas may be proposed for this phenomena. At about 1.8T, spins in Cu(HCOO)(OH) align themselves in almost the same direction, although the alignment is still incomplete. Since increasing field strength further more complete spin alignment, hysteresis observed from this point. That is to say, the saturation occurs through two steps.

$Cu_3(HCOO)_2(OH)_4$

The temperature dependence of magnetic susceptibilities of $Cu_3(HCOO)_2(OH)_4$ is illustrated in Fig. 8. The Xa-T curve shows almost the same behavior as our previous results [1]. Measurements were carried out down to 2K, which was lower than in our previous measurements [1], and the maximum was observed at 2.5K with transition to antiferromagnetic phase. In the curve (Fig. 9), there is little hysteresis. The curve shows irregularity of magnetization, which is characteristic of spin-flop phenomenon; spin-flop field, Hsf, is 1T.

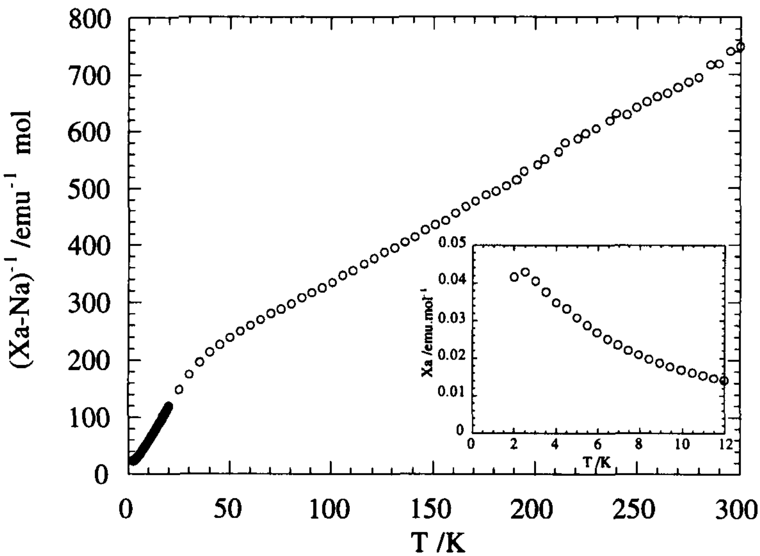

FIGURE 8 Reciprocal magnetic susceptibility of $Cu_3(HCOO)_2(OH)_4$. The insert is temperature dependence of susceptibility (2-12K)

Since trinuclear clusters may function as magnetic units, as reported previously[1], the presence of the maximum at 2.5K in the susceptibility curve(Fig. 8) seems to indicate that intertrimer interaction is antiferromagnetic.

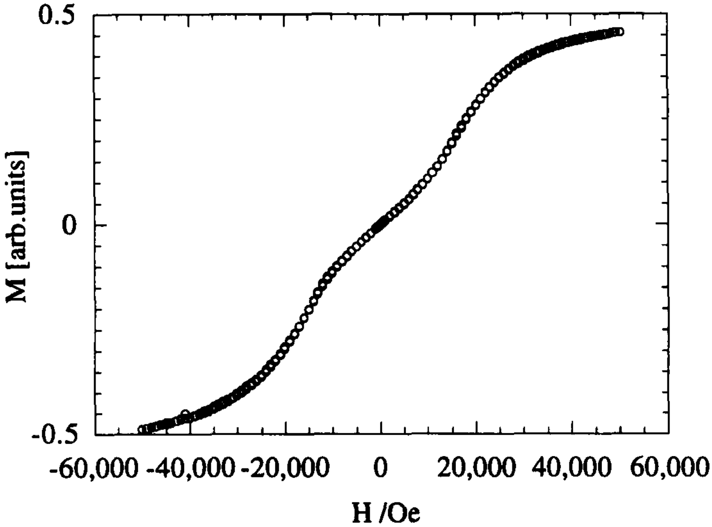

FIGURE 9 Hysteresis curve at 1.8K of $Cu_3(HCOO)_2(OH)_4$.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support of the Ministry of Education, Science and Culture of Japan (Specially Promoted Research No. 06101004).

REFERENCES

1. W. Mori, M. Kishita and M.Inoue, Inorg. Chim. Acta, 42, 11 (1980).
2. H. Tamura, K. Ogawa, W. Mori, M. Kishita, Inorg. Chim. Acta, 54, L87(1981).
3. P. W. Selwood, ' Magnetochemistry', Interscience Publishers, New York, 1956; G. Foex, ' Constants Selectionnes, Diamagnetisme, et Paramagnetisme ', Mason Paris (1957)