COMMUNICATION

Deuterium substitution effects on the structural and magnetic phase transitions of a hydrogen-bonded coordination polymer, bis(glycolato)copper(II)†

Shota Yoneyama,[a] Takeshi Kodama,[a] Koichi Kikuchi,[a] Takumi Fujisawa,[b] Akira Yamaguchi,[b] Akihiko Sumiyama,[b] Yoshiaki Shuku,[c] Shinobu Aoyagi[d] and Wataru Fujita*[d]

Bis(glycolato)copper(II) [Cu(HOCH₂CO₂)₂] shows a structural phase transition around 220 K under cooling and 270 K under heating, and ferromagnetic ordering at 1.1 K. Deuterium substitution of the hydroxyl groups in it induced a large shift in the structural transition temperature while no shift in the ferromagnetic transition temperature took place.

Hydrogen bonds are special intermolecular interactions that give special properties to individual molecules, molecular assemblies, or solids.[1] In particular, in solids, hydrogen bonds induce dielectric properties related to the vibration of a hydrogen atom between electronegative atoms.[2] Ferroelectric and related phenomena have been often observed in materials with hydrogen bonds. Room-temperature ferroelectricity of the organic molecular crystal of croconic acid with a hydrogen bond network had a high impact in the research field of molecular electronic materials.[3] Meanwhile, Mori *et al.* recently advocated new applications of hydrogen bonds in materials sciences.[4] They investigated organic conductors composed of catechol-fused tetrathiafulvalene derivatives and found that deuteration of the hydroxyl groups gave rise to a phase tran-

sition at 185 K, which was accompanied by a large modification of the electrical conductivity and magnetism owing to the motion of deuterium atoms within the hydrogen bonds. This result indicates that hydrogen bonds can be used as a trigger for switching devices in molecule-based electronic materials.

In this study, we have focused on a coordination polymer with hydrogen bonds, bis(glycolato)copper(II) ([Cu(HOCH₂CO₂)₂], (**1**)), whose crystal structure at room temperature was previously reported by Prout *et al.*[5] Fig. 1 shows schematic representation of the crystal structures of **1**. This material forms a two-dimensional square planar lattice network in which two glycolate anions chelate each metal ion *via* the oxygen atoms of their hydroxyl and carboxylate groups, and equatorial Cu–O bonds are formed. In addition, the outer oxygen atoms of the chelate rings coordinate neighbouring complex molecules in the axial direction. Moreover, in this material, there
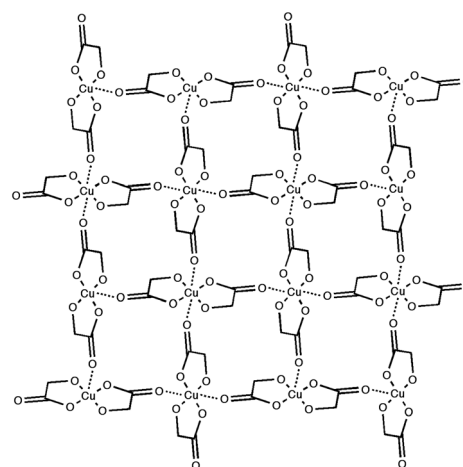
[a]Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, 192-0397, Japan

[b]Department of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan

[c]Department of Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

[d]Department of Information and Basic Science, Nagoya City University, 1 Yamanohata, Mizuho-cho, Mizuho-ku, Nagoya 467-8501, Japan. E-mail: fujitaw@nsc.nagoya-cu.ac.jp; Fax: +81-52-872-5856; Tel: +81-52-872-5856

†Electronic supplementary information (ESI) available: Crystal parameters of the high and low temperature phases in **1–3**, crystal structures of **3**, IR spectra and DSC curves of **1–3** and partially deuterated samples, magnetic analyses for **2** and **3**, differential Fourier maps of the high and low temperature phases in **3**. CCDC 1493335–1493338 for the low and high temperature phases of **2** and **3**, 1507357–1507359 for the partially deuterated samples of 25%, 50% and 75%. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt03592b

Fig. 1 Schematic representation of the coordination polymer bis(glycolato)copper(II) ([Cu(HOCH₂CO₂)₂], **1**) and its two-dimensional square planar lattice network. The broken lines indicate the axial Cu–O bonds.

Dalton Transactions

are intersheet hydrogen bonds formed between the oxygen atoms of the hydroxyl and carboxylate groups (Fig. S1†). Previously, we reported that **1** shows a structural phase transition between the high-temperature (HT) and low-temperature (LT) phases with large thermal hysteresis of approximately 220 K under cooling and 270 K under heating processes, and ferromagnetic ordering at a very low temperature of 1.1 K.[6]

It has been reported that some copper complexes with similar chelate rings show structural phase transitions originating from puckering motions of the chelate rings.[7] Meanwhile, there are some examples of structural phase transitions, in particular, with changes of dielectric properties, that are known to originate from hydrogen bonds.[8] In this study, to investigate the mechanism of the structural phase transition in **1**, we prepared derivatives with deuterium substitution at the methylene group $[Cu(HOCD_2CO_2)_2]$ **2** or the hydroxyl group $[Cu(DOCH_2CO_2)_2]$ **3** (Chart 1), as well as partially substituted derivatives, and structural, magnetic, and thermal analyses of these derivatives were carried out. We found drastic temperature shifts for the structural phase transition upon deuteration of the hydrogen bonds. In addition, we examined the structural phase transition mechanism in the context of these findings.

Fig. 2 shows the results of the magnetic measurements for **2** and **3**. Fig. 2a shows the temperature dependence of the product of the paramagnetic susceptibility and temperature, $\chi_p T$, for the as-prepared sample of **2** under cooling. Compound **2** showed almost the same magnetic behaviour as **1**. As temperatures down to 230 K, the value of $\chi_p T$ was almost constant at 0.466 emu K mol^{-1}, which corresponds to the typical value for Cu(II) ions, calculated from $g = 2.23$ and $S = 1/2$.[9] In the high-temperature region, **2** showed paramagnetism with little magnetic interaction between neighbouring copper ions in the temperature range of 230–400 K. At about 220 K, the $\chi_p T$ value changed discontinuously, indicating a structural phase transition from the HT phase to the LT phase. Notably, this magnetic anomaly at around 220 K was observed in the first cooling of the as-prepared and crystalline samples. After the measurement, the single crystals fractured, in accordance with the large structural change. However, no magnetic anomaly was observed in the ground sample or in the sample heated and cooled several times around this temperature. The inset in Fig. 2a shows the magnetic behaviour during the first cooling from 330 to 190 K and following heating from 190 to 330 K for an as-prepared sample of **2**. The $\chi_p T$ value was about 0.44 emu K mol^{-1} above 220 K, which is
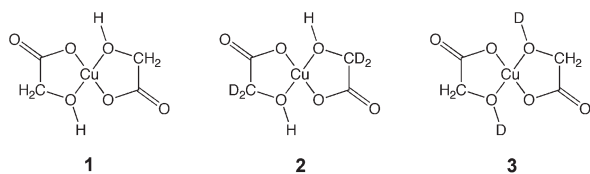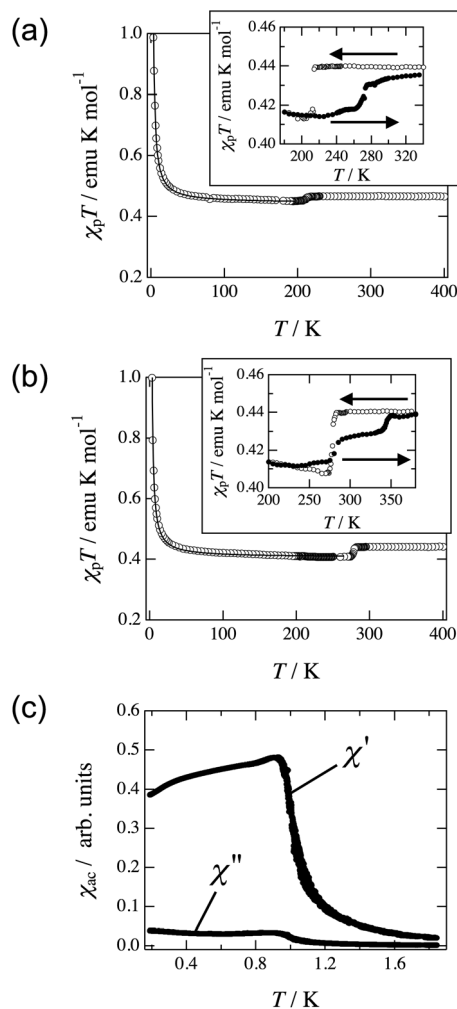

Fig. 2 Magnetic properties of **2** and **3**. (a) Temperature dependence of $\chi_p T$ for **2**. Inset shows thermal hysteresis. The closed and opened circles show the data under cooling and heating processes, respectively. (b) Temperature dependence of $\chi_p T$ for **3**. Inset shows thermal hysteresis. The closed and opened circles show the data under cooling and heating processes, respectively. (c) Temperature dependence of the ac susceptibilities (ac field: 3 mOe, frequency: 500 Hz) of **3** below 1.5 K.

not consistent with the above data of 0.466 emu K mol^{-1}. This may be related to the orientation of the crystals. Thermal hysteresis was observed between the HT and LT phases at approximately 220 K in the cooling process, and gradually at approximately 240–280 K in the heating process. Below 220 K, the $\chi_p T$ value increased with decreasing temperature and reached *ca.* 1 emu K mol^{-1} at 3 K. These results show that the LT phase is paramagnetic with weak ferromagnetic interactions between neighbouring copper ions. The solid line in the temperature range of 2–200 K in Fig. 2a corresponds to the best fit of the theoretical curve corresponding to the $S = 1/2$ two-dimensional square-planar lattice model,[10] with the magnetic parameters of $g = 2.17$ and $2J/k_B = +1.2$ K. These results for **2** indicate that deuteration of the methylene group in **1** has little effect on the structural phase transition and the magnetic properties.

Chart 1 Bis(glycolato)copper(II) **1**, and its deuterium substituted derivatives, **2** and **3**.

Meanwhile, compound **3** shows a magnetic anomaly corresponding to the structural phase transition from the HT phase to the LT phase at 283 K in the $\chi_p T$ *vs.* T plot under cooling (Fig. 2b). Thermal hysteresis and bistability between the HT and LT phases were observed in the temperature range of 280–360 K. The structural phase transition temperature of **3** was 65 K higher than those of **1** and **2**. The magnetic parameters below 280 K were g = 2.08 and $2J/k_B$ = +1.3 K. The inset in Fig. 2b shows the magnetic behaviour during the first cooling from 380 to 200 K, and the subsequent heating from 200 to 380 K for an as-prepared sample of **3**. Thermal hysteresis was also observed for this sample, and the LT phase reverted to the HT phase during the heating process. However, the transition temperature during the heating process could not be determined from the magnetic measurements because of the complex magnetic behaviour. To determine the magnetic ground state and the magnetic transition temperature of **3**, magnetic measurements were carried out below 2 K. Fig. 2c shows the temperature dependence of the real part χ'_{ac} and the imaginary part χ''_{ac} of the ac susceptibilities for **3**. The plots of χ'_{ac} showed an anomaly at 1 K. The value of χ''_{ac} also increased at 1 K, although it became constantly zero above this temperature.[9] This result suggests that a ferromagnetic phase transition occurs at the temperature. The LT phase of **3** showed almost the same magnetic behaviour as **1**. Thus, deuteration of the hydroxyl group in **1** did not affect the magnetic properties, but did have a serious effect on the structural phase transition temperature. Therefore, the hydrogen bonds in **1** play an important role in the structural phase transition.

To estimate the structural phase transition temperatures during cooling and heating of **3**, DSC measurements were carried out. In addition, DSC data were obtained for the 25, 50, and 75% deuterated samples (Fig. S5†). The transition temperatures were estimated from the onset of the exothermic or endothermic peaks observed for each sample. The value of the transition enthalpy in these materials could not be estimated exactly because less thermal contact between samples and sample cells may occur around the transition temperatures. Fig. 3 shows the dependence of the structural phase

transition temperature on the hydroxyl group deuterium substitution ratio. In **3**, the structural phase transition temperatures in the cooling and heating processes were 289 and 349 K, respectively, and a large temperature shift of about 50 K was observed owing to deuteration. The relations between the deuteration ratio and transition temperature were almost linear. A bistability region of approximately 40–60 K was observed, which was tunable in the temperature range of 220–350 K, and the bistability region could be realized at room temperature. Thus, these results suggest that the structural phase transitions observed in **1** and its derivatives are related to the hydrogen bonds. In this study large deuterium isotope effect for the structural phase transition (ΔT = 65 K) of **1** was observed. The result is comparable to the large deuterium isotope effects of ferroelectric phase transitions originated from hydrogen bonds on potassium dihydrogen phosphate KDP (ΔT = 90 K) and $(HDABCO)_2(TCNQ)_3$ (ΔT = 70 K).[11,12]

The structural parameters of the HT and LT phases of **2** and **3** are summarized in Table S1.† The as-prepared samples of these materials were formed as the HT phases. From the DSC measurements, **2** and **3** form bistable states at approximately 230 and 290 K, respectively, and thus the crystal structures of both phases can be determined at the same temperature. The X-ray structure analyses of **2** were carried out using the as-prepared crystal for the HT phase and after cooling the sample to 180 K for the LT phase. The structural data for **3** were obtained at 290 K, using the as-prepared sample for the HT phase and a single crystal first cooled in liquid nitrogen for the LT phase. The HT and LT phases of **2** and **3** were isostructural with the corresponding phases of **1**.[6] However, there were large differences among the lattice constants; in particular, there were more than 1 Å difference between the *b* and *c* axes in the HT and LT phases of these materials. Fig. 4 shows the molecular alignments of the HT and LT phases of **3** at 290 K. The coordination networks of both phases are of the same type as those of **1**, as shown in Fig. 1. However, the molecular orientation in the LT phase is different from that in the HT phase. In addition, in the HT phase, each copper complex molecule is
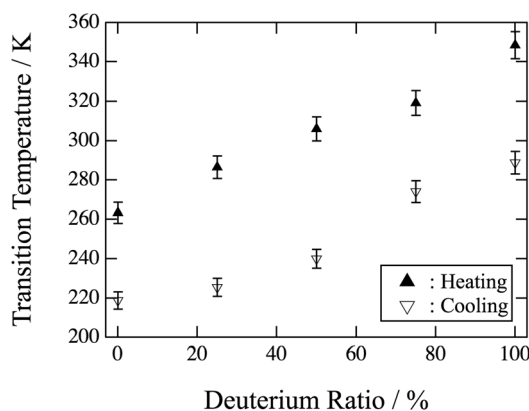
Fig. 3 Relation between the structural phase transition temperature and deuterium substitution ratio.
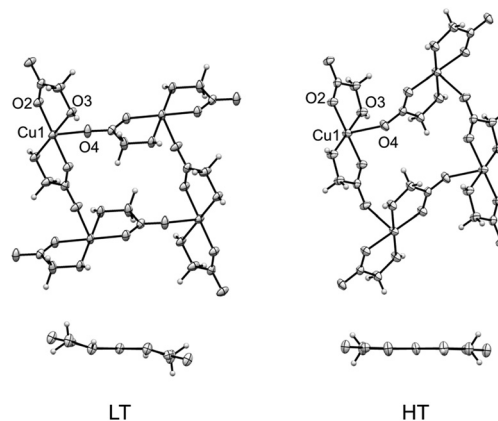
Fig. 4 Molecular shape and arrangement of copper complex molecules in the LT and HT phases of **3**.

almost flat, but a slight bend in the molecular plane at the oxygen atoms of the chelate rings is observed in the LT phase. The same structural differences were observed between the HT and LT phases of **2**. A ferromagnetic interaction occurred between the copper ions in **2** and **3**, as well as in **1**.[6] In these materials, the copper atoms are bridged by carboxylate groups with one oxygen atom of the carboxylate ion coordinated to the equatorial position of the copper ion, and the other oxygen atom coordinated to the axial position of the neighbouring copper ion. It is known that such a magnetic interaction path gives rise to ferromagnetic interactions.[13]

Fig. 5 shows schematic representations of the local structures around the hydrogen bonds in the LT and HT phases. There are no significant differences in the interatomic O3···O4 distances in the hydrogen bonds of the LT and HT phases in **3** at 290 K. However, the axial Cu1–O4 coordination bond length in the LT phase was *ca.* 0.1 Å shorter than that in the HT phase. Meanwhile, the equatorial Cu1–O3 bond length in the LT phase was *ca.* 0.02 Å longer than that in the HT phase. To estimate the position of the deuterium atom in the hydrogen bond, difference Fourier maps in the LT and HT phases of **3** were estimated from the structural models, not including hydrogen or deuterium atoms (Fig. S6†). The electron density peaks in both phases, which correspond to an electron of the deuterium atom, were found between the oxygen atoms. The distances between the electron density peak and O3 were 0.87 and 0.95 Å in the LT and HT phases, respectively. Thus, there is clear difference in the electron density peak positions. As shown in Fig. 5, the OD bond length in the HT phase seems to be longer than that in the LT phase.

Based on the above structural differences between the LT and HT phases, the mechanism of the structural phase transition in these materials can be discussed. In general, a hydrogen atom in a hydrogen bond is positively charged and vibrates between the oxygen atoms. The vibrational state and position of the hydrogen atom are dependent on parameters such as the temperature. At lower temperatures, the hydrogen atom exists in its energy minimum. However, at higher temperatures, the hydrogen atom vibrates thermally between the oxygen atoms, resulting in the elongation of the O3–H(D) bond, as shown in Fig. 5. Thus, the hydrogen atom in the HT

phase is closer to O4 than that in the LT phase. In these materials, it seems that the axial Cu1–O4 bond is especially sensitive to the position of the hydrogen atom. When the distance between the hydrogen and oxygen atoms becomes shorter, the ligand field of the oxygen atom may become weaker owing to the positive charge of the hydrogen atom. Thus, the Cu–O bond may elongate. The large elongation of the axial Cu–O bond leads to an orientation change of the molecular units in the complex. For these reasons, it is thought that the structural phase transition is triggered by the thermal motion of the hydrogen atoms in the hydrogen bonds and by the elongation of the axial Cu–O bonds.

In summary, deuterium substitution effects on the structural and magnetic phase transitions of a coordination polymer, bis(glycolato)copper(ɪɪ), were examined. Deuteration of the hydroxyl groups in **1** induced a large temperature shift for the structural phase transition, but a small temperature shift for the ferromagnetic phase transition. The origin of the structural phase transition is related to a combination of the position of the hydrogen atom in the hydrogen bond and the bond length of the axial Cu–O bond. In general, superexchange interactions between transition metal ions bridged by ligands are sensitive to structural modification of their bridging structures. The experimental results obtained in this study suggest that the magnetic properties of materials with hydrogen bonds may depend on the state of the hydrogen bonds. Although little magnetic modifications were observed in **1–3** because of very weak magnetic interactions between copper ions, hydrogen-bonded coordination polymers with strong magnetic interactions may be magnetically sensitive to external stimuli, such as pressure, electric field, and heat. If their hydrogen bonds affect bridging structures between transition metal ions and modify their magnetic properties, they will be useful for magnetic materials whose magnetic properties can be controlled by external stimuli.[14] Currently, we are exploring such magnetic materials, named "H-bonded magnets" (Fig. S7†).
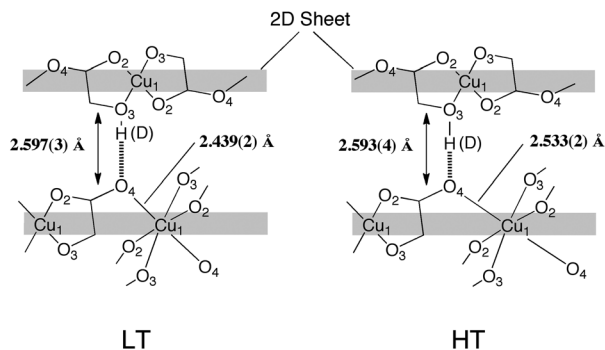
Fig. 5 Schematic representations of the structures around the hydrogen bonds in the LT and HT phases of **3**.

Notes and references

1 L. Pauling, *The Nature of Chemical Bond*, Cornell University Press, New York, 3rd edn, 1960; G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, Reinhold Publishing Corporation, New York, 1960; G. A. Jeffrey, *An Intorduction to Hydrogen Bond*, Oxford University Express, Oxford, 1997; G. Gilli and P. Gilli, *The Nature of the Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory (IUCr Monocgraphs on Crystallography 23)*, Oxford University Express, Oxford, 2013.

2 F. Jona and G. Shirane, *Ferroelectric Crystals (International Series of Monographs on Solid State Physics)*, Pergamon Press, 1962.

3 S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai and Y. Tokura, *Nature*, 2010, **463**, 789.

4 A. Ueda, S. Yamada, T. Isono, H. Kamo, A. Nakao, R. Kumai, H. Nakao, Y. Murakami, K. Yamamoto, Y. Nishio and H. Mori, *J. Am. Chem. Soc.*, 2014, **126**, 12184; J. Yoshida, A. Ueda, A. Nakao, R. Kumai, H. Nakao, Y. Murakami and H. Mori, *Chem. Commun.*, 2014, 15557; A. Ueda, A. Hatakeyama, R. Kumai, Y. Murakami and H. Mori, *Chem. – Eur. J.*, 2015, **21**, 15020.

5 C. K. Prout, R. A. Armstrong, J. R. Carruthers, J. G. Forrest, P. Murray-Rust and F. J. C. Rossotti, *J. Chem. Soc. A*, 1968, 2791; Q.-S. Ye, M. J. Xie, W. P. Liu, X.-Z. Chen, Q.-W. Chang and Y. Yu, *Z. Kristallogr. – New Cryst. Struct.*, 2010, **225**, 481.

6 S. Yoneyama, T. Kodama, K. Kikuchi, Y. Kawabata, K. Kikuchi, T. Ono, Y. Hosokoshi and W. Fujita, *CrystEngComm*, 2013, **15**, 10193.

7 I. Grenthe, P. Paoletti, M. Sandstroem and S. Glikberg, *Inorg. Chem.*, 1979, **18**, 2687; K. Takahashi, R. Nakajima, Z. Gu, H. Yoshiki, A. Fujishima and O. Sato, *Chem. Commun.*, 2002, 1578.

8 Y. Moritomo, S. Koshihara and Y. Tokura, *J. Chem. Phys.*, 1990, **93**, 5429; A. Katrusiak and M. Szafránski, *Phys. Rev. Lett.*, 1999, **82**, 576; P. Jain, V. Ramachandran, R. J. Clark, H. D. Zhou, B. H. Toby, N. S. Dalal, H. W. Kroto and A. K. Cheetham, *J. Am. Chem. Soc.*, 2009, **131**, 13625.

9 L. R. Carlin, *Magnetochemistry*, Springer-Verlag, Berlin, 1986.

10 G. A. Baker, H. E. Gilbert, J. Eve and G. S. Rushbrooke, *Phys. Lett. A*, 1967, **25**, 207.

11 N. Ichikawa, K. Motida and N. Yamada, *Phys. Rev. B: Condens. Matter*, 1987, **36**, 874.

12 T. Akutagawa, S. Takeda, T. Hasegawa and T. Nakamura, *J. Am. Chem. Soc.*, 2004, **126**, 291.

13 Y.-H. Liu, S.-H. Lee, J.-C. Chiang, P.-C. Chen, P.-H. Chien and C.-I. Yang, *Dalton Trans.*, 2013, **42**, 16857.

14 O. Sato, *Nat. Chem.*, 2016, **8**, 644.