Large structural transformation and ferromagnetic ordering in a coordination polymer with a two-dimensional square-planar lattice, bis(glycolato)copper(II)†

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A coordination polymer with a two-dimensional square planar lattice network, bis(glycolato)copper(II), shows a large structural phase transition at around 220 K and ferromagnetic ordering at 1.1 K.

Coordination polymers of transition-metal ions show unique magnetic properties such as high-T_c ferri/ferromagnetism, photomagnetism, single-chain quantum magnetism, chiral magnetism, magnetic bistability, and guest-induced magnetic changes.[1–6] Bis(glycolato)metal(II), $[M(C_2H_3O_3)_2]$ (M = Co, Ni, and Cu), which has been reported by some research groups,[7] has a coordination polymer structure. Fig. 1 shows schematic representations of the molecular and crystal structures of these materials. Two glycolate anions chelate to a metal ion *via* the oxygen atoms of their hydroxyl and carboxylate groups, and equatorial Cu–O bonds are formed. The outer oxygen atoms of the chelate rings in the complex molecule coordinate to neighbouring complex molecules toward the axial direction, and a two-dimensional square-planar lattice network is formed. It is expected that magnetic interactions between the metal ions work *via* the carboxylates and that unique magnetic behaviours are induced in these materials. However, there have been no magnetic studies of these derivatives. In this study, we demonstrate structural transformation with large thermal hysteresis and ferromagnetic ordering in the copper derivative, bis(glycolato)copper(II), *i.e.* $[Cu(C_2H_3O_3)_2]$ (**1**).

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Compound **1** was prepared as follows. An aqueous solution (100 mL) containing 1.3 g of copper acetate monohydrate and 1 g of glycolic acid was kept at 80 °C for several hours. After gradual cooling of the solution to room temperature and allowing it to stand for several hours, light-blue block crystals were obtained. The chemical composition of **1** was determined by X-ray structure analyses.

Fig. 2 shows the results of some magnetic measurements of **1**. Fig. 2a shows the temperature dependence of the product of the paramagnetic susceptibility and temperature, $\chi_p T$, of **1** in the temperature range of 0.5–400 K under a magnetic field of 500 Oe. Down to 230 K, the value of $\chi_p T$ was almost constant at 0.457 emu K mol^{-1}, which corresponds to the typical value of a Cu(II) ion calculated from $g = 2.21$ and $S = 1/2$.[8] In the high-temperature region, this material showed Curie paramagnetism, which refers to the absence of magnetic interactions between neighbouring copper ions in the temperature range of 230–400 K. At 220 K, the $\chi_p T$ value changed discontinuously, indicating a structural phase transition. The inset to Fig. 2a shows the first cooling and heating processes for an as-prepared sample in the temperature range of 200–300 K. Thermal hysteresis was observed, accompanying the phase transition of the high-temperature phase to the low temperature phase at about 220 K in the cooling process and the gradual phase transition of the low-temperature phase to the high temperature phase at around 240–280 K in the heating process. After the magnetic measurements, single crystals of **1** were broken into small pieces.

The magnetic anomaly with thermal hysteresis was only observed in the first cooling and heating processes of the as-prepared sample but did not appear after multiple cooling and heating processes. DSC experiments on the sample indicated exothermic peaks at around 220 K and endothermal peaks at around 270 K after multiple cooling and heating processes, respectively. This indicates that the structural phase transition takes place not only in the as-prepared sample but also in the sample that underwent multiple cooling
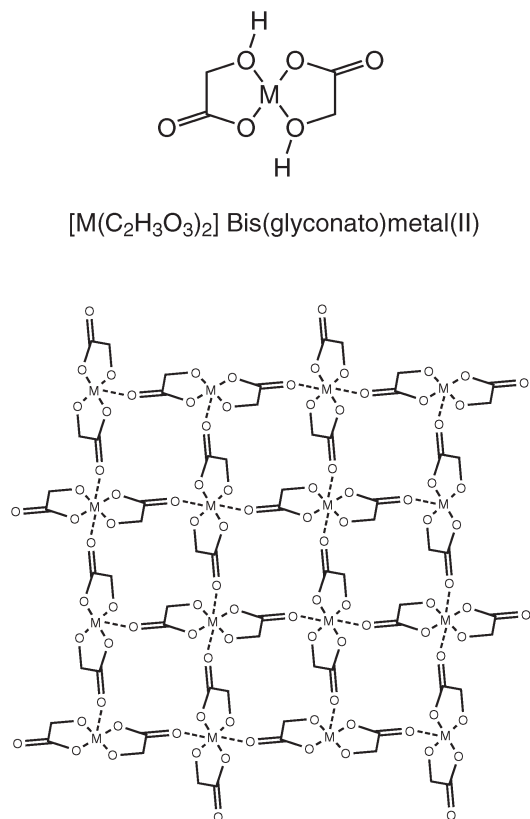
[M(C₂H₃O₃)₂] Bis(glyconato)metal(II)

Fig. 1 Schematic presentation of a coordination polymer with a two-dimensional square planar lattice network, bis(glycolato)₂metal(ɪɪ) [M(C₂H₃O₃)₂] (M = Co, Ni, and Cu).

Fig. 2 Magnetic properties of **1**. (a) Temperature dependence of $\chi_p T$. Inset shows thermal hysteresis. (b) Temperature dependence of the ac susceptibilities (ac field 1 Oe, frequency 1 Hz) below 1.5 K. (c) Field dependence of magnetization at 0.5 K.

and heating treatments. Below 220 K, the $\chi_p T$ value increased with decreasing temperature and reached *ca.* 1.8 emu K mol⁻¹ at 2 K. These results show that the low-temperature phase is paramagnetic with a weak ferromagnetic interaction between neighbouring copper ions.[8] The solid line in the temperature range of 2–200 K in Fig. 2a corresponds to the best fit of the theoretical curve of the $S = 1/2$ two-dimensional square-planar lattice model,[9] with the magnetic parameters $g = 2.09$ and $2J/k_B = +1.4$ K. The magnetic interaction in the low-temperature phase is stronger than that in the high-temperature one.

In order to determine the magnetic ground state and the magnetic transition temperature of **1**, magnetic measurements were carried out below 2 K. Fig. 2b shows the temperature dependence of the real part χ_{ac}' and the imaginary part χ_{ac}'' of the ac susceptibilities for **1** under an applied field of 1 Oe (1 Hz) and a dc field of 0 Oe. The plots of χ_{ac}' showed anomalies at 1 K. The value of χ_{ac}'' also increased at 1.1 K, although it was constantly zero above this temperature. This suggests the appearance of a ferromagnetic component in this material.[8] Fig. 2c shows the *M–H* curve measurement of **1** at 0.5 K, where the magnetization value increased under a lower magnetic field and was almost saturated at 1000 Oe. The magnetization value at 50 000 Oe was 5892 erg Oe⁻¹ mol⁻¹, which is extremely close to the theoretical value for the ferromagnetic ordered state of 1 mol of the $S = 1/2$ spin
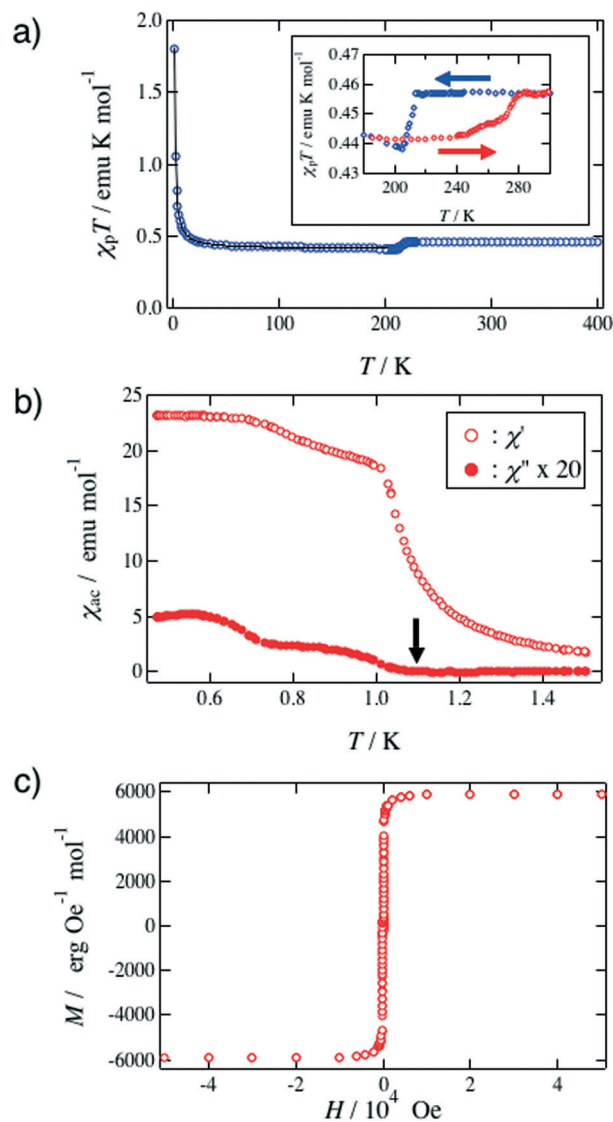
material.[8] It is concluded that the low-temperature magnetic data indicate ferromagnetic ordering with $T_c = 1.1$ K. The presence of a negligibly small hysteresis loop with a width less than 10 Oe indicates that the obtained material is a soft magnet. Two-dimensional magnetic materials with a square-planar lattice network showing ferromagnetic ordering are very rare; they have been found in tetrahalogenocuprate salts, A_2CuX_4 (A: cations, X: F or Cl).[10] The transition temperature of **1** is lower than those of the tetrahalogenocuprate salts, $T_C = 6$–10 K. The magnetic interaction *via* the carboxylate ion is weaker than those *via* halogen ions.

To investigate the origin of the magnetic anomaly at around 220 K, we carried out X-ray crystal structure analyses in the high- and low-temperature regions. Table 1 summarizes the crystal parameters of this material at 250 K and 150 K. It crystallized in the monoclinic $P2_1/n$ space group.

Table 1 Crystal parameters of **1** at 250 K and 150 K

	250 K	150 K
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	5.0908(8)	5.178(4)
b/Å	8.6939(12)	7.208(5)
c/Å	7.7300(14)	8.889(7)
β/°	107.141(8)	100.840(9)
V/Å^3	326.93(10)	325.8(5)
Z	2	2
R_1 ($I > 2\sigma$)	0.0255	0.0457
wR_2 (all data)	0.0640	0.1166

There are large differences among the lattice constants, in particular, a more than 1 Å difference between the b and c axes. Fig. 3 shows the molecular alignments of the complex molecules at 250 K and 150 K. The high-temperature phase had the same structure as this material at 298 K, as reported previously by Ye *et al.*[7d] In the low-temperature phase, the two-dimensional coordination network between Cu(II) ions *via* the carboxylate group was maintained. 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. In this case, it is known that the exchange interaction related to the $d_{x^2-y^2}$ and d_{z^2} orbitals *via* ligands becomes ferromagnetic.[11] The molecular orientation at 150 K was drastically different from that in the high-temperature phase. Also, at 250 K, the complex molecule was almost flat, but a slight bending of the molecular plane at the oxygen atoms of the chelate rings was observed at 150 K. The axial Cu–O coordination bond length at 150 K was 2.432(4) Å, which is about 0.1 Å shorter than that at 250 K. It is known that shrinkage of the axial bond leads to enhancement of magnetic interactions between the magnetic ions because of increased overlap between the d_{z^2} orbital and the ligand orbital,[12] *i.e.* magnetic interaction

in the low-temperature phase may be stronger than that in the high-temperature phase. This is consistent with the results of the magnetic measurements. Thus, the structural phase transition in **1** originated from a change in the molecular orientation, shrinkage of the axial coordination bond lengths, bending of the molecular plane, and so on.

In conclusion, we report a preparation method, a large structural phase transition with a small magnetic change, and ferromagnetic ordering in the coordination polymer **1**, which has a two-dimensional square-planar lattice network. The magnetic phases are summarized below. Ferromagnetic ordering in a magnetic material with a two-dimensional square planar lattice network is rare. It is interesting that a structural change accompanying the expansion or contraction of a coordination bond leads to a magnetic modification of the material. Further investigations of the magnetic and structural properties of materials related to **1**, including those with other metal ions and chemically modified ligands, are currently in progress.
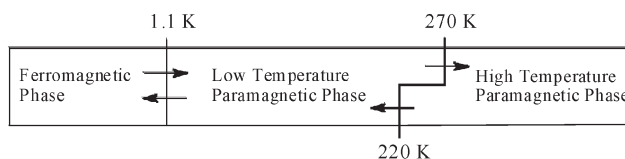
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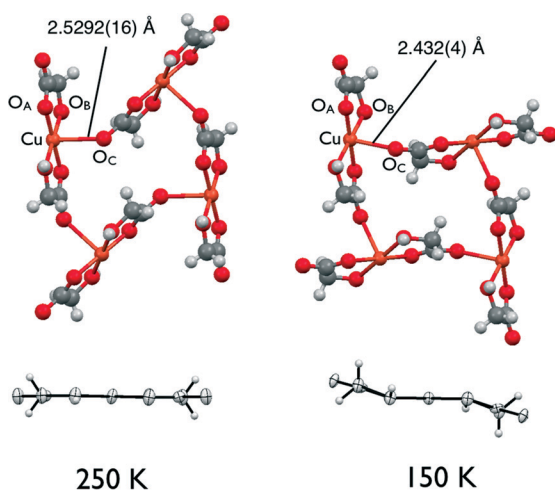
Fig. 3 Molecular shape and arrangement of the copper complex molecules in **1** at 250 K and 150 K. Selected bond lengths (Å) at 250 K: Cu–O$_A$, 1.9222(18); Cu–O$_B$, 1.935(2); Cu–O$_C$, 2.5292(16). At 150 K: Cu–O$_A$, 1.934(4); Cu–O$_B$, 1.959(4); Cu–O$_C$, 2.432(4).

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