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# Introduction

Coordination polymers exhibit unique magnetic properties such as high- $T_c$  ferri/ferromagnetism, photomagnetism, single-chain quantum magnetic, magnetic bistabilities, and guest-induced magnetic changes.<sup>1</sup> Recently, we have reported that a coordination polymer, bis(glycolato)copper(II) [Cu(HOCH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>], exhibited a structural phase transition between its high-temperature and low-temperature phases; this phase transition was associated with a large thermal hysteresis of approximately 220 K upon cooling and 280 K upon heating, with ferromagnetic ordering at 1.1 K.<sup>2</sup> Deuterium substitution in the hydroxy groups induced a large 220 K to 280 K

# Magnetic, thermal, and neutron diffraction studies of a coordination polymer: bis(glycolato)cobalt(n)

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The two-dimensional quadratic lattice magnet, bis(glycolato)cobalt(II) ([Co(HOCH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>]), showed antiferromagnetic ordering at 15.0 K and an abrupt increase in magnetisation at  $H = 22\,600$  Oe and 2 K, thereby acting as a metamagnet. Heat capacity measurements revealed that the associated entropy change  $\Delta S$  around the transition temperature was evaluated to be 6.20 J K<sup>-1</sup> mol<sup>-1</sup> and that the Co(II) ion had the total angular momentum of J = 1/2 at low temperatures. Neutron diffraction studies suggested that the magnetic moment vectors of the Co(II) ions had an amplitude of  $3.59\mu_{\rm B}$  and were not aligned in a fully antiparallel fashion to those of their neighbours, which caused canting between the magnetic moment vectors in the sheet. The canting angle was determined to be 7.1°. Canting induced net magnetisation in the sheet, but this magnetisation was cancelled between sheets. The magnetisations in the sheets were oriented parallel to the magnetic field at the critical magnetic field.

shift in the structural transition temperature upon cooling, while no shift in the ferromagnetic transition temperature was observed.<sup>3</sup> The origin of the structural phase transition was attributed to the positions of hydrogen atoms in hydrogen bonds.

In this work, we focused on a coordination polymer, bis(glycolato)cobalt(II) ([Co(HOCH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>], 1), whose crystal structure had previously been reported by Medina *et al.*;<sup>4</sup> this material is isostructural with the copper derivative  $[Cu(HOCH_2CO_2)_2]$ . Fig. 1 shows a schematic representation of the crystal structure of 1. This material has a two-dimensional lattice network comprising Co(II) ions coordinated equatorially to two glycolate anions in a bidentate fashion through hydroxy and carboxylate oxygen atoms, and axially to two glycolate carbonyl oxygen atoms, to form coordination sheets (Fig. 1(a)). The planes of the five-membered chelate rings are roughly perpendicular with respect to each other. There are O-H…O hydrogen bonds between hydroxy hydrogen atoms and the outer carbonyl oxygen atoms of the carboxylates in the intersheets, as shown in Fig. 1(b). Magnetic interactions between Co(II) ions are expected to occur via the carboxylates, so that 1 shows a unique magnetic behaviour. However, there have been no magnetic studies or structural analyses at various temperatures such as those established for the Cu derivative. Hence, we investigated the magnetic and thermal properties of 1, as well as its magnetic anomaly at 15.0 K and the anomalous field dependence of magnetisation at 2 K. We also elucidated the origin of the magnetic anomaly by means of neutron diffraction studies.



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**Fig. 1** Schematic representation of the coordination polymer bis(glycolato)cobalt(II) ( $[Co(HOCH_2CO_2)_2]$ , **1**). (a) The structure of the coordination sheet. The sheets are parallel to the (1 0 –1) plane. The broken lines indicate the axial Co–O bonds. (b) Atomic alignment of the hydrogen bond formed between intersheets.

## Experimental

Compound 1 was prepared following a reported procedure.<sup>4</sup> Accordingly, 100 mL of an aqueous solution containing 2.00 g (8.03 mmol) of cobalt acetate tetrahydrate and 1.23 g (16.1 mmol) of glycolic acid was maintained at 90 °C for 13 d. At the end of this period, dark reddish block crystals were obtained. Single crystals were grown to a maximum size of 5.0 mm × 2.0 mm × 2.0 mm (Fig. S1†). Anal. Calcd for  $C_4H_6O_6Co_3$ : C, 22.98%; H, 2.89%; found: C, 23.02%; H, 2.89%.

Magnetic studies were performed on a polycrystalline sample, which was prepared by crushing single crystals of **1**, at temperatures down to 2 K using a Quantum Design Co. Ltd MPMS SQUID magnetometer. The raw experimental data were corrected for the diamagnetic susceptibility of **1** ( $-81.22 \times 10^{-6}$  emu mol<sup>-1</sup>) as determined from Pascal's constants.<sup>5</sup> The molar unit of paramagnetic susceptibility  $\chi_{\rm p}$  was chosen as the quantity per mole of Co(HOCH<sub>2</sub>COO)<sub>2</sub>.

Heat-capacity measurements were carried out for a block crystal on a Quantum Design physical property measurement system (PPMS) equipped with a relaxation-type calorimeter. Data were corrected for the sample mount and the Apiezon grease used to hold the sample on the mount. The molar unit of the heat capacity  $C_{\rm p}$  was chosen as the quantity per mole of Co(HOCH<sub>2</sub>COO)<sub>2</sub>. The specific heat capacity  $C_{\rm mag}$  was obtained by subtracting the lattice contribution from the total heat capacity  $C_{\rm p}$ . The lattice heat capacity  $C_{\rm lattice}$  was determined from the  $C_{\rm p}$  data in the 30–50 K temperature range using the following equation:

$$C_{\rm p} = aT^3 + bT^5 + cT^7 + dT^9 + eT^{-2}, \tag{1}$$

where the last term stands for the high-temperature limit of the specific heat capacity,<sup>6</sup> and the remaining terms correspond to the lattice heat capacity  $C_{\text{lattice}}$ . The coefficients obtained following fitting were: a = 0.001047,  $b = -6.5835 \times 10^{-7}$ ,  $c = 2.1773 \times 10^{-10}$ ,  $d = -2.8193 \times 10^{-14}$ , and e = 1129.1. The magnetic entropy was obtained by integrating  $(C_{\rm p} - C_{\text{lattice}})/T$  in the 0–50 K temperature region.

Neutron diffraction experiments were carried out on a SENJU (BL 18) MLF, J-PARC single-crystal TOF neutron diffractometer.7 The J-PARC accelerator power was 200 kW. The data were collected at wavelengths of 0.4-4.0 Å (1st frame) at 298 K, 25 K (> $T_N$ ), and 5 K (< $T_N$ ). The crystal structure was first analysed at 300 K to verify the quality of a single crystal. The crystal structures were then re-determined at 25 K and 5 K in order to examine the structural phase transitions in the 5-300 K temperature range, and to locate magnetic peaks below the magnetic-transition temperature. Experiments at 5 K were also carried out at wavelengths of 4.0-8.0 Å (2nd frame) in order to collect magnetic peaks in the low Q-range. Diffraction data were processed using the STARGazer datareduction program to provide HKL-F data.8 Crystal and magnetic-structure analyses were performed using the JANA2006 programs.9 Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1876541-1876543 for compound 1 at 5 K, 20 K and 298 K, respectively).

# Results and discussion

#### **Magnetic properties**

Fig. 2 shows the results of magnetic measurements carried out on **1**. Fig. 2(a) displays the paramagnetic susceptibility  $(\chi_p)$  of **1** as a function of temperature, measured in a magnetic field of 50 Oe. The  $\chi_p$  value increased gradually with decreasing temperature, reaching a sharp maximum at 15.2 K, after which it decreased rapidly below this temperature, which is suggestive of a magnetic phase transition. Fig. 2(b) shows the  $\chi_{\rm p}T$  vs. T plot of 1; the  $\chi_p T$  value was 3.006 emu K mol<sup>-1</sup> at 300 K. A gradual decrease in the  $\chi_{\rm p}T$  value was observed upon cooling. Data in the 150-300 K range were fitted to the Curie-Weiss law,<sup>5</sup> with C = 3.476 emu K mol<sup>-1</sup> and  $\theta = -44.3$  K, where C and  $\theta$  are the Curie and Weiss constants, respectively. The effective magnetic moment was determined to be  $5.27\mu_{\rm B}$  from the Curie constant, which is consistent with that expected for a high spin state in an octahedral Co(II) ion, as proposed by Mabbs and Machin,<sup>10</sup> who also proposed that an isolated octa-



Fig. 2 Magnetic properties of **1**. (a) Temperature dependence of the paramagnetic susceptibility  $\chi_p$  for non-oriented microcrystals under 50 Oe. (b) The  $\chi_p T$  vs. T plot for non-oriented microcrystals. The solid curves indicate the theoretical best fits of the Curie–Weiss law. (c) Field dependence of the magnetization for non-oriented microcrystals of **1** at 2 K and 25 K.

hedral Co(II) ion has a Weiss constant  $\theta$  of -20 K, which results in a gradual transformation of the total angular momentum quantum number (J = 3/2) at high temperature to J = 1/2 at low temperature.<sup>10</sup> The  $\theta$  value of -44.3 K for **1** suggests spin-orbit coupling in each Co(II) ion; furthermore, it indicates that antiferromagnetic interactions arise between Co(II) ions *via* carboxylate groups that link the molecules in the complex.

Kurmoo *et al.* reported the magnetic properties of bis(mandelato)cobalt( $\pi$ ), where mandelate is a phenyl-substituted  $\alpha$ -hydroxycarboxylate.<sup>11</sup> Although this material also forms a two-dimensional quadratic coordination sheet similar to that observed for **1**, magnetic interactions between Co( $\pi$ ) ions were weak and no magnetic phase transition was observed down to

2 K. On the other hand,  $Co(HCOO)_2 \cdot 2H_2O$  is also a coordination polymer in which  $Co(\pi)$  ions are bridged by carboxylates, although the bridging structure is different.<sup>12</sup> In this material, antiferromagnetic interactions exist between the  $Co(\pi)$  ions, and an antiferromagnetic phase transition is observed at 5.4 K, which suggests that the strengths of the superexchange interactions *via* the carboxylate groups influence the bridging structure.

Fig. 2(c) shows the dependence of magnetisation on the field at 2 and 25 K. At 25 K, which is above the magnetic transition temperature, magnetisation increases linearly with the increasing magnetic field. At 2 K, below the magnetic transition temperature, magnetisation also increases linearly in the lower magnetic-field region. A rapid increase in magnetisation, of ~2300 erg  $Oe^{-1}$  mol<sup>-1</sup>, was observed at around a magnetic field of 22 600 Oe. Once again, magnetisation increased linearly at fields above 25 000 Oe. The magnetisation of 1 reached ~5000 erg  $Oe^{-1}$  mol<sup>-1</sup> at 70 000 Oe and was not saturated. This behaviour is similar to those observed for metamagnets.<sup>5</sup>

#### Heat capacity

Fig. 3 shows the temperature dependence of the heat capacity  $(C_p)$  of **1** in the 2–50 K temperature range. The heat capacity exhibits an anomaly at 15.0 K, which supports the existence of magnetic ordering at this temperature. The total magnetic entropy was evaluated to be 6.20 J K<sup>-1</sup> mol<sup>-1</sup> by integrating  $C_p/T$  with respect to *T*. This value is similar to the expected  $\Delta S$  value for the magnetic ordering of 1 mol with J = 1/2 ( $R \ln(2J + 1) = 5.76$  J K<sup>-1</sup> mol<sup>-1</sup>).<sup>13</sup> This result indicates that an octahedral Co(II) ion has a total angular momentum quantum number of J = 1/2 in the ground state. This is consistent with the literature<sup>11</sup> and with the magnetic behavior shown in this work.

#### Neutron diffraction

We investigated **1** by neutron diffraction at 5 K, 20 K, and 298 K, and determined its crystallographic and magnetic structures. The structural parameters summarised in Table 1 are based on neutron diffraction data and are consistent with the results from the X-ray diffraction studies.<sup>4</sup> There are no signifi-



Fig. 3 Temperature dependence of the heat capacity  $C_p$  for 1.

T/K	298 K	20 K	5 K
Crystal system	Monoclinic		
Space group	$P2_1/n$		
a/Å	5.180(3)	5.170(3)	5.143(3)
b/Å	7.860(5)	7.697(5)	7.656(5)
c/Å	8.659(5)	8.701(5)	8.653(5)
β/Å	105.129(8)	104.492(8)	104.429(8)
$V/Å^3$	340.3(4)	335.2(4)	330.0(3)
Ζ	2	2	2
$R_1$	0.0783	0.0680	0.0692
$wR_2$	0.1070	0.1116	0.1235

cant structural differences among the Co–O coordination bond lengths, O–H bond lengths, or O–H···O (hydrogen bond) interatomic distances over the investigated temperature range (Tables S1 and S2†). We previously reported that the structural phase transition of bis(glycolato)copper( $\pi$ ) [Cu(HOCH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>] is triggered by the thermal motion of hydrogen atoms in hydrogen bonds and the elongations of axial Cu–O bonds.<sup>3</sup> In this study, compound **1** showed no structural phase transition in the 2–300 K temperature range; the Co( $\pi$ ) ions do not undergo large Jahn–Teller distortions and possess elongated axial bonds. This suggests that hydrogen bonds and elongated coordination bonds, which are affected by the positive charges of protons, play important roles, as observed during the structural phase transition of the copper derivative.

At 5 K, magnetic reflections with a propagation vector q =(0.5 0 0.5) were observed, as shown in Fig. S2.<sup>†</sup> The unit cell volume of the magnetic structure is twice as large as that of the crystal structure, which is characteristic of antiferromagnetic ordering. The magnetic structure is described by the  $P2_1/c$  magnetic space group with a  $(-a + b) \times b \times (-a - b)$ supercell. Magnetic structure analyses were performed using 555 magnetic reflections (334  $(I > 3\sigma)$ ); this refinement gave reliable factors, namely R = 11.76% and wR = 21.63%. Fig. 4 shows the magnetic structure of 1 at 5 K. The green arrows correspond to the magnetic moment vectors of Co(II) ions; their magnitudes of  $3.59(7)\mu_{\rm B}$  are consistent with those of Co(II) ions in octahedral environments.<sup>11</sup> The magnetic moments are almost parallel to the coordination sheet and are not aligned in an exactly antiparallel fashion with their neighbours, which causes canting toward the *b* axis in the sheet. The canting angle to the neighbouring vector was determined to be 7.1°. Although the canting of magnetic moments is found in many Co(II) compounds,<sup>14</sup> their magnetic structures have rarely been determined by neutron diffraction using single crystals.

We next interpreted the anomalous field dependence of this material below the transition temperature. Fig. 5 shows a schematic representation of the magnetic structure and magnetisation of the coordination sheets in **1**. Because of the antiferromagnetic ordering in the material at 15.0 K, the magnetic moment vectors of the Co(n) ions are aligned in an antiparallel fashion. A divalent cobalt ion in an octahedral environment has a highly anisotropic *g*-tensor arising from spin–orbit coup-





**Fig. 4** Magnetic structure for **1** at 2 K. The blue, red, brown and white spheres are cobalt, oxygen, carbon and hydrogen atoms. The green arrows are magnetic moment vectors. The unit cell is of the crystal structure.



**Fig. 5** Schematic presentation of (a) rearrangement of magnetic moment vectors on Co(II) ions in the coordination sheet. Blue spheres are cobalt ions. Green arrows are the magnetic moment vectors. Red arrows indicate the direction of the magnetization in the coordination sheet. Direction of magnetization in the coordination sheets for **1** at 2 K (b) below  $H_c$  and (c) above  $H_C$ .

ling.<sup>5</sup> The molecules in the complex are oriented in two ways (Fig. 1(a)), and each complex molecule has its own axis of easy magnetisation. Based on the orientation of the molecules in

the complex and their magnetic moment vectors, canting occurs due to a competition between antiparallel alignments that cause antiferromagnetic interactions, and the anisotropies of the Co(II) ions. As a result, a small net magnetisation occurs in the coordination sheet toward the b axis, as shown in Fig. 5(a). Hence, each coordination sheet is spontaneously magnetised toward the b axis, and magnetisation cancels out in the intersheets (Fig. 5(b)). It is likely that weak antiferromagnetic interactions occur between the sheets via the hydrogen bonds.<sup>15</sup> The magnetisation in each sheet of this material is oriented toward the magnetic field below the critical field of 22 600 Oe (Fig. 5(c)). As shown in Fig. 2(c), a rapid increase of  $\sim$ 2300 erg Oe<sup>-1</sup> mol<sup>-1</sup> in magnetisation was observed. The magnetisation can be calculated to be 2480 erg  $Oe^{-1}$  mol<sup>-1</sup> from the magnetic moment of  $3.59\mu_{\rm B}$ , determined from the neutron diffraction experiments, and the canting angle of 7.1°, which is consistent with the observed rapid increase; the assumption shown in Fig. 5 is supported by this value. The magnetisation increases with the increasing magnetic field above the critical magnetic field because the canting angle increases.

## Conclusions

We carried out magnetic, thermal, and neutron diffraction studies on the coordination polymer, bis(glycolato)cobalt(II)  $([Co(HOCH_2CO_2)_2])$ . This material showed antiferromagnetic ordering at 15.0 K and a rapid increase in magnetisation at  $H = 22\,600$  Oe at 2 K. This magnetic behaviour was similar to that of a traditional metamagnetic material. Neutron diffraction studies revealed that the cobalt derivative did not exhibit large structural changes with temperature and, hence, there was no structural phase transition, unlike the  $Cu(\pi)$  species which exhibited a structural phase transition that originated from hydrogen-bonds. We successively determined the magnetic structure of 1 at 5 K and explained its magnetic behaviours in detail. The magnetic moments on the  $Co(\pi)$  ions are not aligned in an exactly antiparallel fashion with their neighbours, which results in canting between magnetic moment vectors; this canting induces net magnetisation in the sheets. Weak antiferromagnetic interactions occur between the sheets and the magnetisation is cancelled out between them. The magnetisation in the sheet is orientated toward the magnetic field above the critical magnetic field, which is why this material shows metamagnetic behaviour.

# Conflicts of interest

There are no conflicts to declare.

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