Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Large Structural Transformation and Ferromagnetic Ordering in Coordination Polymer with Two-dimensional Square Planar Lattice, Bis(glycolato)copper(II)

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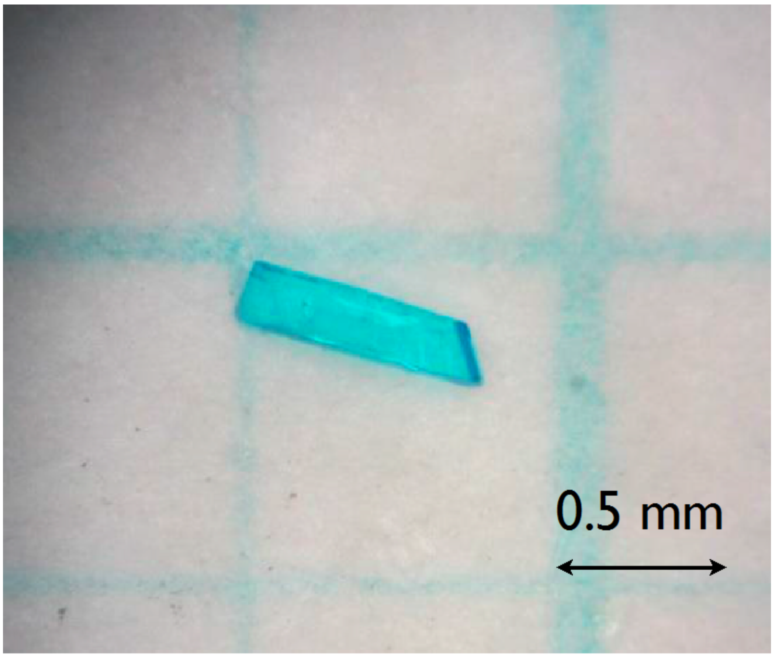
1. Photograph

a)



b)

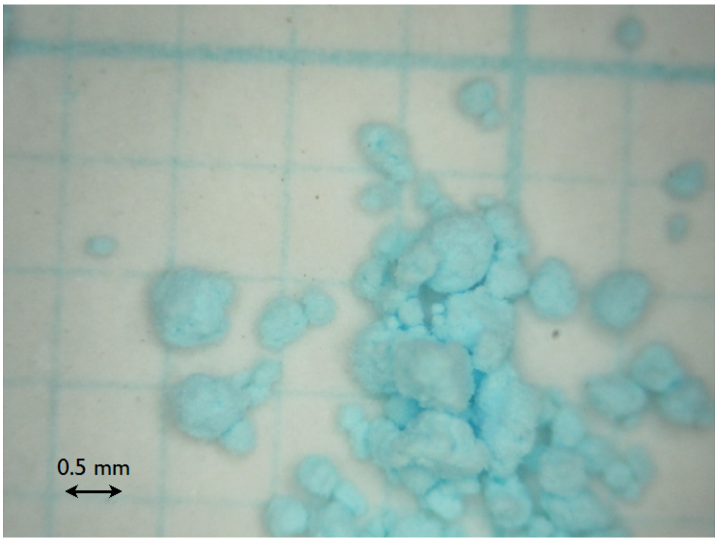


Figure S1. Photographs of **1**. (a) the as-prepared sample. (b) after the magnetic measurements.

2. X-ray Measurements and Analyses of 1

X-ray diffraction data were collected with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation on a RIGAKU Mercury CCD diffractometer. Temperature control was carried out using Digital X-ray Cryo System XR-CS190D (Japan Thermal Engineering Co. Ltd.). All structures were solved by a direct method using the SHELXS-90 program[1] and refined by successive differential Fourier syntheses and a full-matrix least-squares procedure using the SHELXL-97 program.[2] Anisotropic thermal factors were applied to all non-hydrogen atoms. CCDC-950567 and 950568 at 150 K and 250 K, respectively, contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S1. Crystal structural parameters of **1** at 150 K and 250 K.

	150 K	250 K
CCDC ID code	950567	950568
Empirical formula	$C_4H_6CuO_6$	$C_4H_6CuO_6$
Formula weight	213.64	213.64
Color	light blue	light blue
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	5.178(4)	5.0908(8)
b (Å)	7.208(5)	8.6939(12)
c (Å)	8.889(7)	7.7300(14)
β□(deg)	100.840(9)	107.141(8)
V (Å3)	325.8(5)	326.93(10)
Z	2	2
Dcalcd (g cm^{-3})	2.177	2.170
μ (mm^{-1})	3.330	3.319
Index range	$-6 \leq h \leq 6$	$-6 \leq h \leq 6$
	$-9 \leq k \leq 9$	$-11 \leq k \leq 7$
	$-9 \leq l \leq 11$	$-10 \leq l \leq 9$
Reflections collected	732	743
Goodness-of fit on F^2	1.118	1.183
$R1$, $wR2$ (all data)	0.0727, 0.1166	0.0310, 0.0640
Temperature (K)	150(1)	250(1)

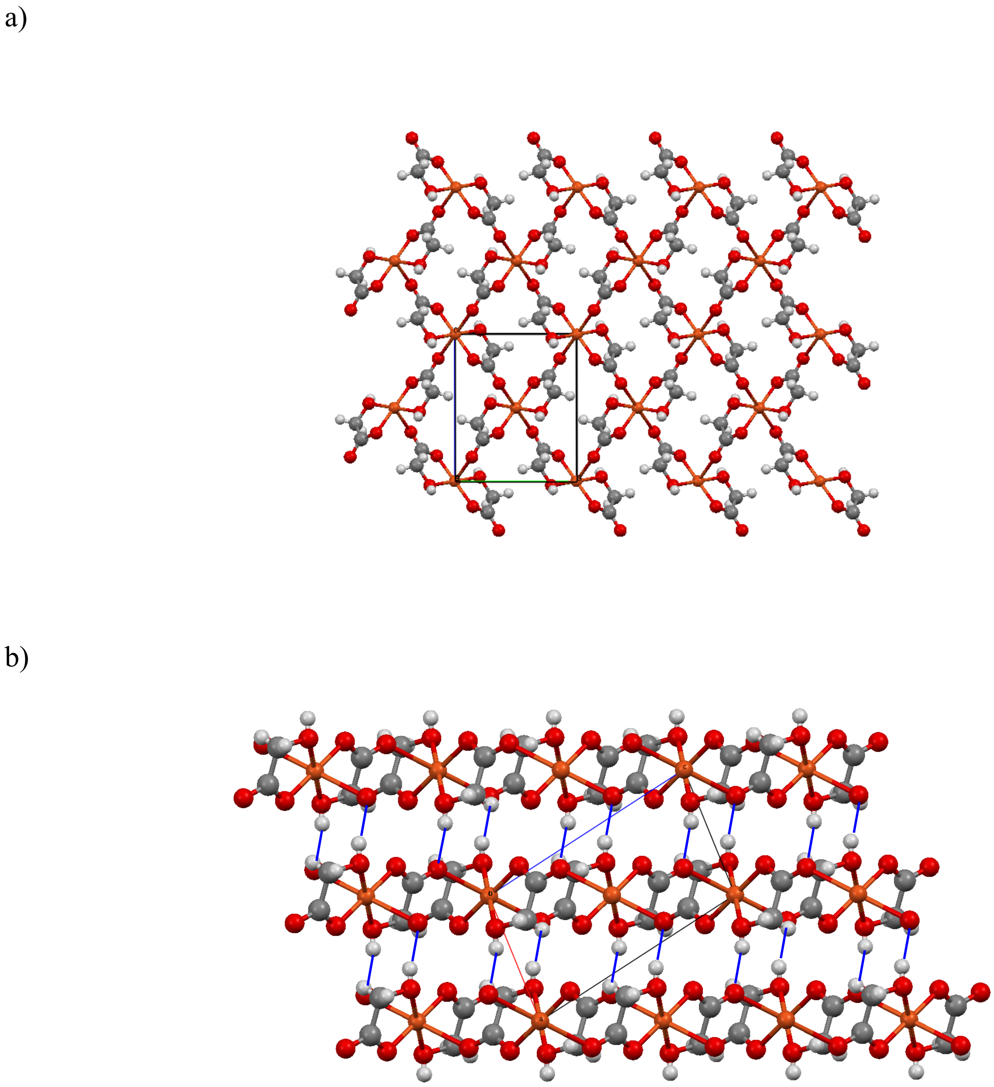


Figure S2. Crystal structure of **1** at 150 K. (a) Projection of the coordination network toward the *a* axis. (b) Stacking fashion of the coordination sheets toward the *b* axis. There are hydrogen bonds between the coordination sheets (blue solid lines). The O•••O distance was 2.604(6) Å.

3. Magnetic Measurements of 1

Magnetic measurements of **1** were carried out for an as-prepared sample on a SQUID (Quantum Design MPMS XL) magnetometer down to 1.8 K and in combination with a ^{3}He refrigerator for $0.5\ \mathrm{K} < T < 1.8\ \mathrm{K}$. Temperature dependence of the dc susceptibility was measured under 500 Oe above 2 K and under 20 Oe below 2 K. The experimental raw data were corrected for the diamagnetic contribution, –0.0001586 emu mol^{-1}, which was estimated by assuming that the magnetic behavior of **1** above 230 K follows the Curie law. Field dependence of magnetization of **1** was carried out at 0.5 K. The ac magnetic measurements were carried out under an applied field of 1 G (1 Hz) for the ac field and 0 G for the dc field.

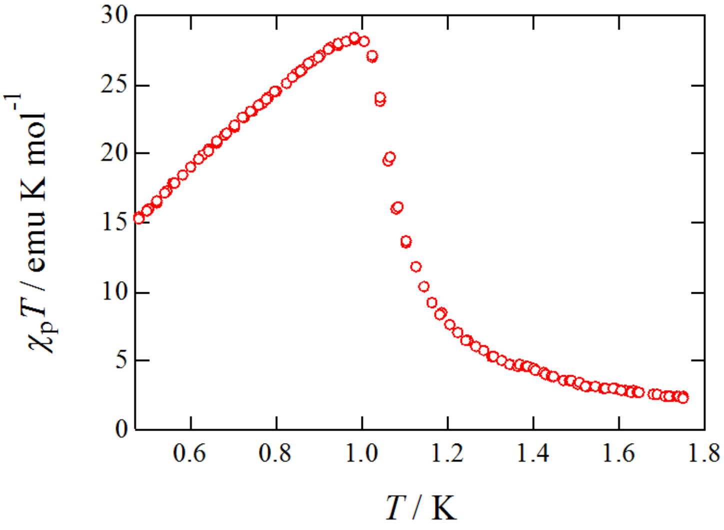


Figure S3. Temperature dependence of $\chi_p T$ for **1** under the dc magnetic field of 20 Oe below 2 K.

After multiple cooling down to 200 K and heating up to 310 K, the magnetic anomaly was disappeared in the sample as shown in Fig. S4. However, the structural phase transition took place because endothermic and exothermic peak were observed from DSC measurements as shown in Fig. S6 of Section 4. After multiple cycles, the as-prepared crystals became powder, as described in our manuscript. Then, we tried to measure magnetic properties of a well-grinding sample of the as-prepared crystals and estimated that little magnetic anomaly was disappeared in that, as shown in Fig. S5. We think that the origin of magnetic anomaly is related to orientation of the crystals.

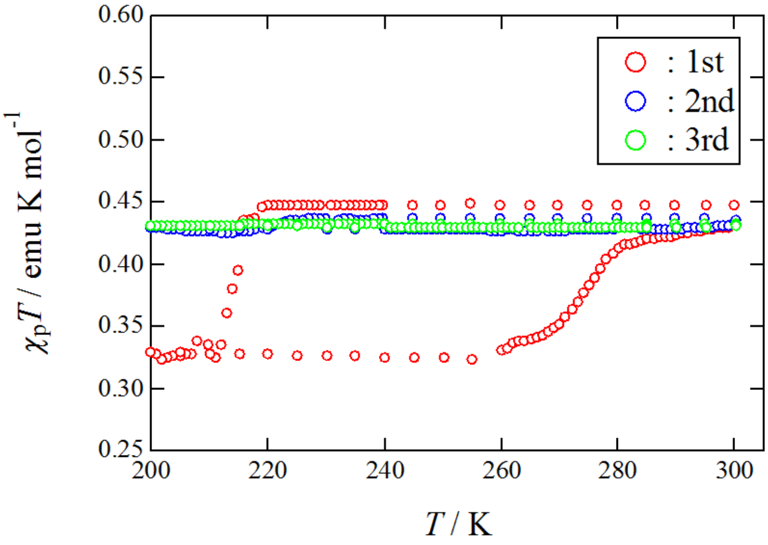


Figure S4. Temperature dependence of χ_pT for **1** under the dc magnetic field of 500 Oe. Red, blue, and green circles corresponds to the magnetic data for the first, second, and third cooling and heating, respectively.

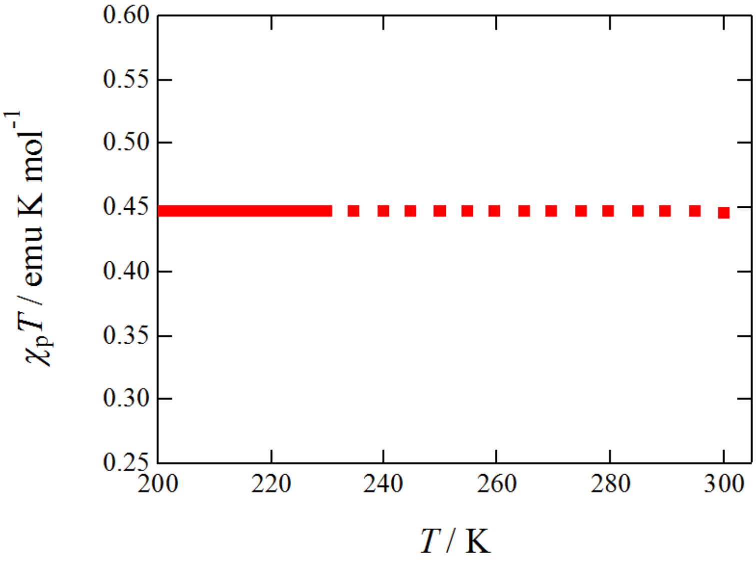


Figure S5. Temperature dependence of χ_pT for the grinding sample of **1** under the dc magnetic field of 500 Oe.

4. DSC Measurements

The DSC measurements were performed on a Rigaku Thermo Plus 2 Series DSC 8230L calorimeter. Cooling and heating rates were –5 K min^{-1} and 5 K min^{-1}, respectively.

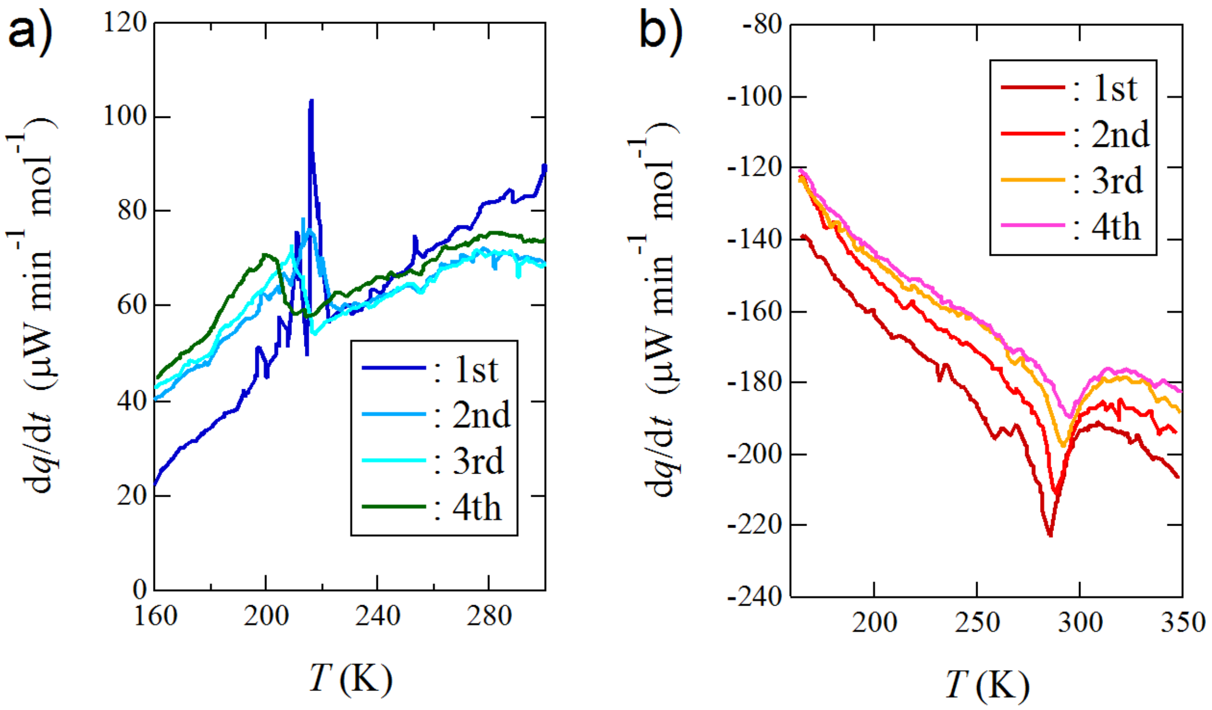


Figure S6. DSC curves for **1** upon (a) cooling and (b) heating.

5. Powder X-ray Diffraction Measurements

Powder X-ray diffraction data of an as-prepared sample and the sample after multiple cooling down to 77 K and heating up to 310 K were collected with graphite-monochromated Cu-Kα (λ = 1.51 Å) radiation on a RIGAKU Multiflex X-ray diffractometer at room temperature.

Table S1. Some peak positions of powder X-ray diffraction patterns for an as-prepared sample and the sample after the thermal treatment, and calculated from single crystal data at 250 K and 150 K in **1**. This result means that the sample returned to the high-temperature phase at room temperature after the thermal treatment.

As-prepared (RT)	After the thermal treatment (RT)[a]	High-temperature phase (250 K)[b]	Low-temperature phase (150 K)[c]
15.68	15.68	15.74	15.94
18.60	18.59	18.65	18.46
20.83	20.84	20.92	20.34
23.73	23.73	23.75	21.38
23.96	23.96	24.10	25.11
24.56	24.55	24.70	27.26
26.62	26.63	26.78	31.94
27.58	27.56	27.64	32.21
32.14	32.14	32.26	33.19
35.89	35.89	36.10	38.74
40.50	40.27	40.52	40.75

a The sample was cooled down to 77 K and heated up to 313 K, several times.

b Calculated from single crystal data of the sample at 250 K.

c Calculated from single crystal data of the sample at 150 K.

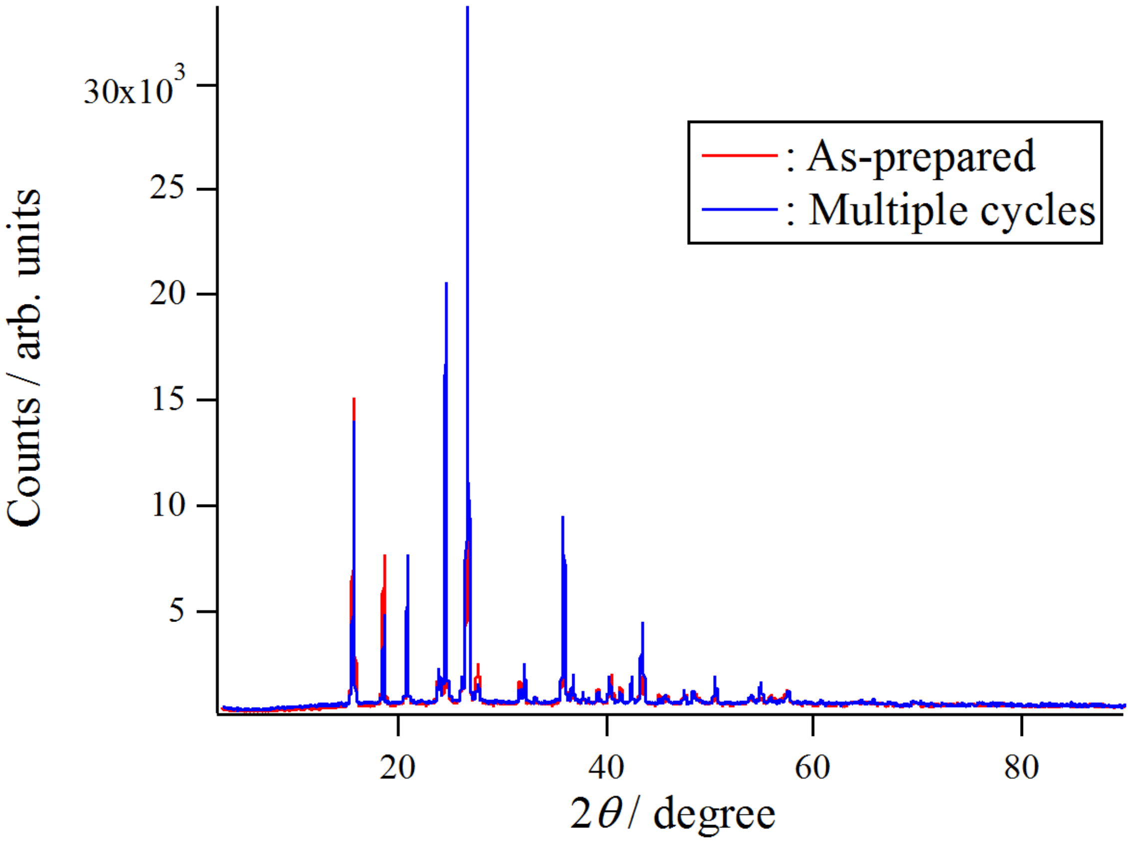


Figure S7. Powder X-ray diffractions of (1) the as-prepared sample and (2) the sample after the thermal treatment at room temperature.

6. References

1. G. M. Sheldrick, *Acta Crystallogr. A* 1990, **46**, 467.
2. G. M. Sheldrick, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.