Supporting Information

Preparation, Crystal Structure, and Magnetic Properties of Copper Hydroxy Salt with Diamond Chain Magnetic Network

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1. X-ray Measurements and Analyses of 1 and its Polymorph β.

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. 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** and its polymorph β at 250 K.

|	**1**	β
CCDC ID code	1015729	1026061
Empirical formula	$C_{16}H_{26}Cu_3O_{16}S_4$	$C_{16}H_{26}Cu_3O_{16}S_4$
Formula weight	793.25	793.25
Color	light blue	light blue
Crystal system	triclinic	triclinic
Space group	$P–1$	$P–1$
a (Å)	5.712(4)	9.523(5)
b (Å)	8.741(6)	14.450(6)
c (Å)	27.100(16)	20.410(9)
α (deg)	97.596(9)	71.148(14)
β (deg)	91.516(6)	79.669(17)
γ (deg)	100.966(10)	76.292(15)
V (Å^3)	1314.8(15)	2566(2)
Z	2	4
Dcalcd (g cm^{-3})	1.842	1.861
Reflections collected	4439	8741
Goodness-of fit on F^2	1.041	1.032
$R1$, $wR2$ (all data)	0.0479, 0.1330	0.0625, 0.1830

(a)
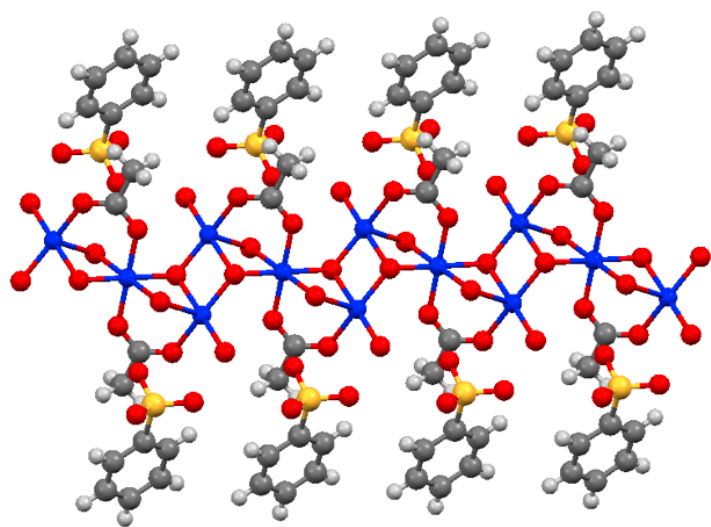
(b)
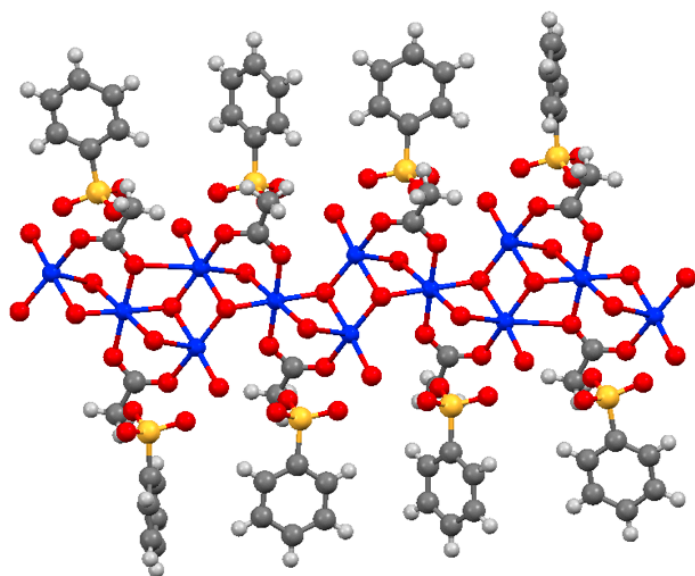
Figure S1. Structural comparison of **1** with its polymorph β. Atomic alignment of (a) **1** and (b) the β phase. Hydrogen, light grey; carbon, dark grey; oxygen, red; copper, blue; sulfur, yellow. The polymorph β has also a distorted diamond chain magnetic network.
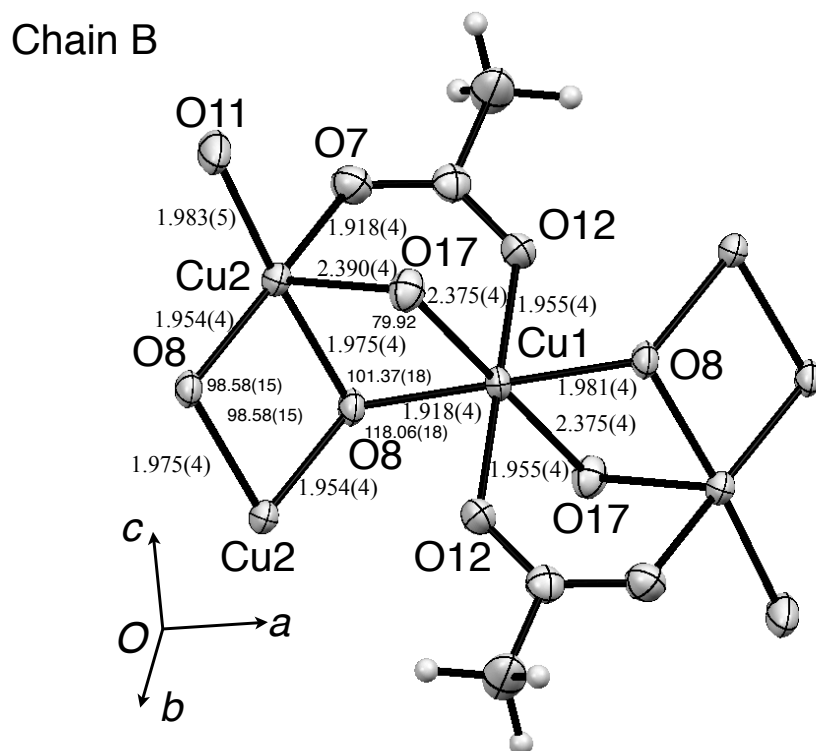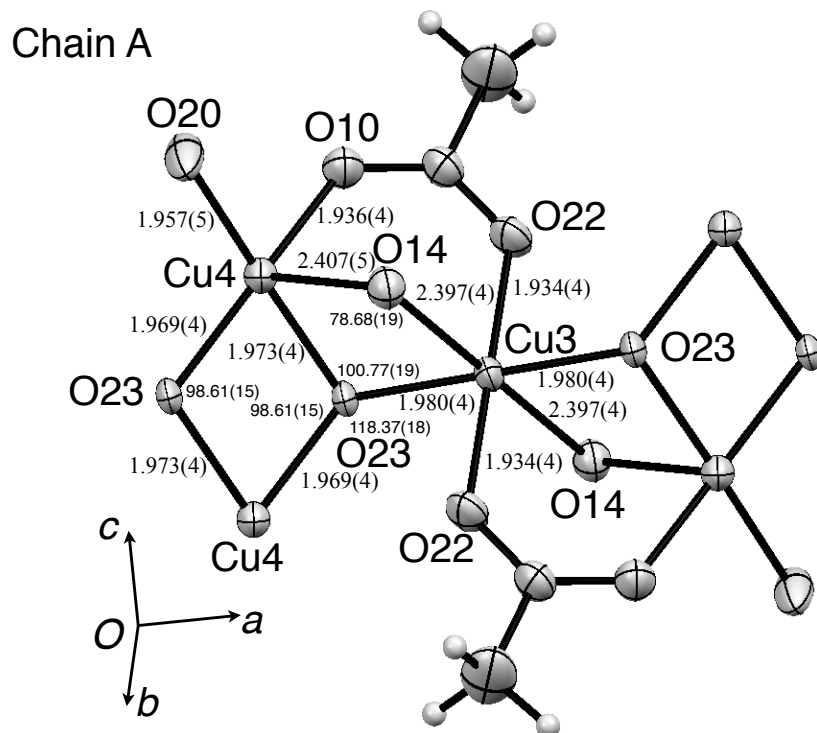
Figure S2. Local structures, main interatomic distances and bond angles in the copper hydroxide chain units A and B in **1**. Interatomic distances and bridging angles were described in Times New Roman and Helvetica, respectively.

Table S2. Interatomic distances (Å) of the copper hydroxide chain units A and B in **1**.

atom	atom	distance	atom	atom	distance
Cu1	O8	1.981(4)	Cu3	O22	1.934(4)
Cu1	O12	1.955(4)	Cu3	O23	1.980(4)
Cu1	O17	2.375(4)	Cu3	O14	2.397(4)
Cu2	O7	1.918(4)	Cu4	O10	1.936(4)
Cu2	O8	1.975(4)	Cu4	O20	1.957(5)
Cu2	O8	1.954(4)	Cu4	O23	1.973(4)
Cu2	O11	1.983(5)	Cu4	O23	1.969(4)
Cu2	O12	2.811(5)	Cu4	O22	2.839(5)
Cu2	O17	2.390(4)	Cu4	O14	2.407(5)

Table S3. Cu–O–Cu bridging angles (^{o}) of the copper hydroxide chain units A and B in **1**.

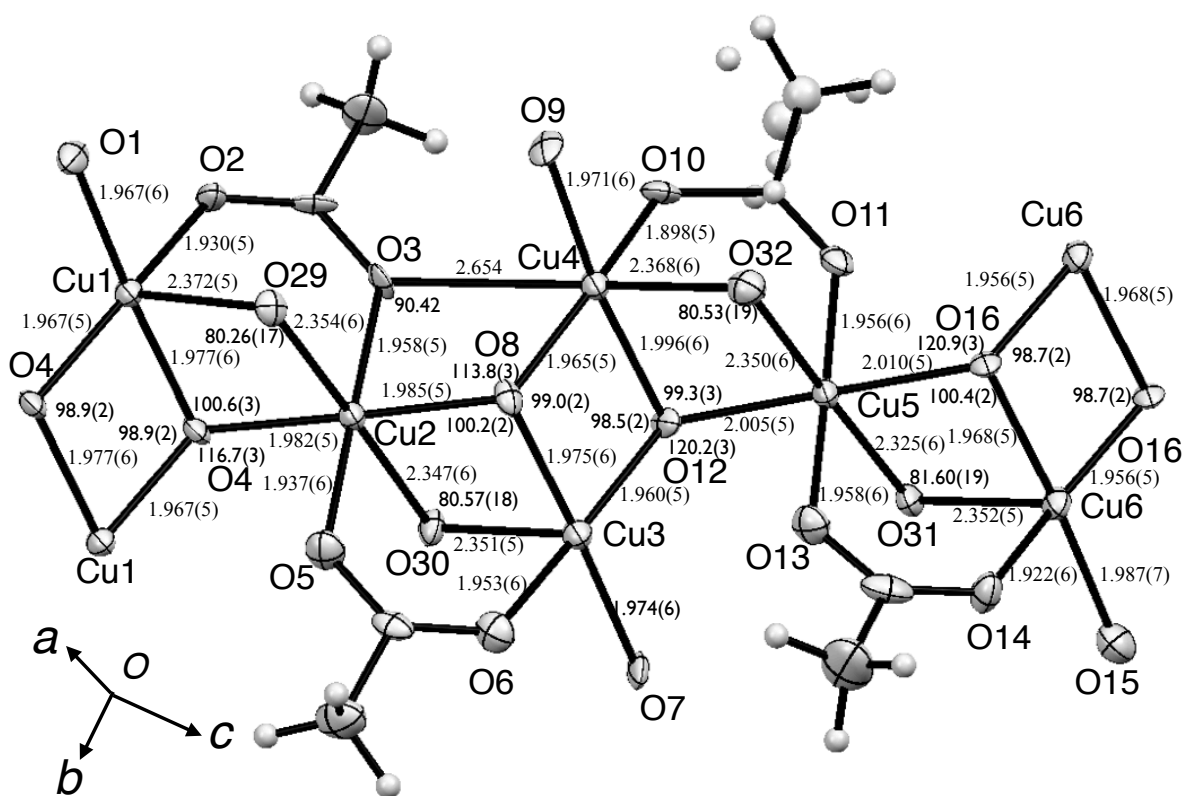| atom	atom	atom	angle	atom	atom	atom	angle
Cu1	O8	Cu2	101.37(18)	Cu3	O23	Cu4	100.77(19)
Cu1	O8	Cu2	118.06(18)	Cu3	O23	Cu4	118.37(18)
Cu2	O8	Cu2	98.58(15)	Cu4	O23	Cu4	98.61(15)

Figure S3. Local structures, main interatomic distances and bond angles in the copper hydroxide chain unit of the β phase. Interatomic distances and bridging angles were described in Times New Roman and Helvetica, respectively.   One carboxylate group has a static disorder.

Table S4. Interatomic distances (Å) of the copper hydroxide chain units in the β phase.

atom	atom	distance	atom	atom	distance
Cu1	O2	1.930(5)	Cu4	O10	1.898(5)
Cu1	O1	1.967(6)	Cu4	O8	1.965(5)
Cu1	O4	1.967(5)	Cu4	O9	1.971(6)
Cu1	O4	1.977(6)	Cu4	O12	1.996(6)
Cu1	O29	2.372(5)	Cu4	O32	2.368(6)
Cu2	O5	1.937(6)	Cu5	O11	1.956(6)
Cu2	O3	1.958(5)	Cu5	O13	1.958(6)
Cu2	O4	1.982(5)	Cu5	O12	2.005(5)
Cu2	O8	1.985(5)	Cu5	O16	2.010(5)
Cu2	O30	2.347(6)	Cu5	O31	2.325(6)
Cu2	O29	2.354(6)	Cu5	O32	2.350(6)
Cu3	O6	1.953(6)	Cu6	O14	1.922(6)
Cu3	O12	1.960(5)	Cu6	O16	1.956(5)
Cu3	O7	1.974(6)	Cu6	O16	1.968(5)
Cu3	O8	1.975(6)	Cu6	O15	1.987(7)
Cu3	O30	2.351(5)	Cu6	O31	2.352(5)

Table S5. Cu–O–Cu bridging angles (º) of the copper hydroxide chain units in the β phase.

atom	atom	atom	angle	atom	atom	atom	angle
Cu1	O4	Cu1	98.9(2)	Cu2	O29	Cu1	80.26(17)
Cu1	O4	Cu2	116.7(3)	Cu2	O30	Cu3	80.57(18)
Cu1	O4	Cu2	100.6(3)	Cu5	O31	Cu6	81.60(19)
Cu4	O8	Cu3	99.0(2)	Cu5	O32	Cu4	80.53(19)
Cu4	O8	Cu2	113.8(3)	Cu4	O12	Cu5	99.3(3)
Cu3	O8	Cu2	100.2(2)	Cu6	O16	Cu6	98.7(2)
Cu3	O12	Cu4	98.5(2)	Cu6	O16	Cu5	120.9(3)
Cu3	O12	Cu5	120.2(3)	Cu6	O16	Cu5	100.4(2)

2. Powder X-ray Diffraction Measurements of 1

Powder X-ray diffraction data of an as-prepared sample were collected with graphite-monochromated Cu-Kα (λ = 1.54056 Å) radiation on a RIGAKU RINT UltimaIII X-ray diffractometer at room temperature.

Table S6. Major peak positions (2θ / °) of powder X-ray diffraction patterns for **1** at room temperature and calculated from single crystal data at 250 K in **1**.

1, measured (RT)	**1**, calculated (250 K)[a]	**1**, measured (RT)	**1**, calculated (250 K)[a]
6.540	6.58	25.820	25.80
8.320[b]	—	26.720	26.82
10.460	10.46	31.260	31.28
11.281	11.34	33.179	33.12
13.280	13.32	34.561	34.68
15.280	15.34	37.140	37.18
18.180	18.22	37.839	37.76
19.780	19.84	40.260	40.28
20.860	20.90	41.000	40.96
21.840	21.88	42.100	42.14
22.741	22.80	42.701	41.78
23.121	23.14	43.741	43.86
24.040	24.08	45.222	45.20
24.882	24.86	47.679	47.74

a Calculated from single crystal data of **1** at 250 K.

b This peak did not correspond to **1** or the β phase and attributes to small amount of impurity.
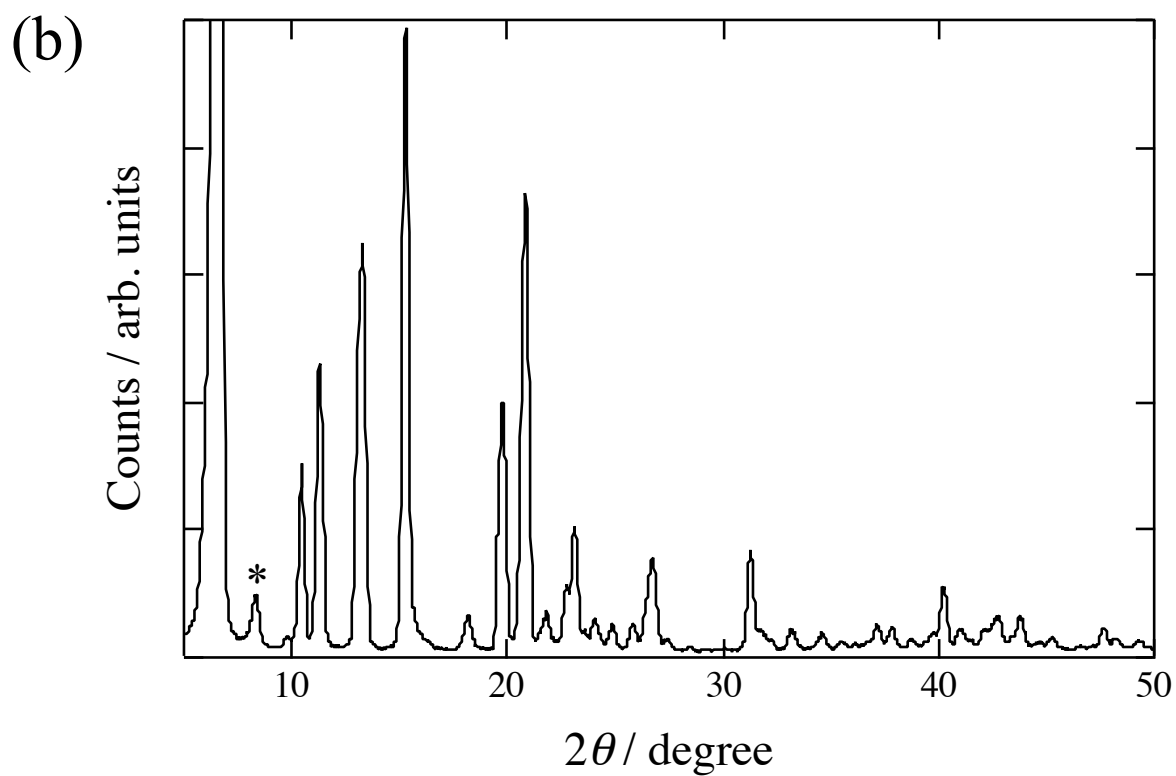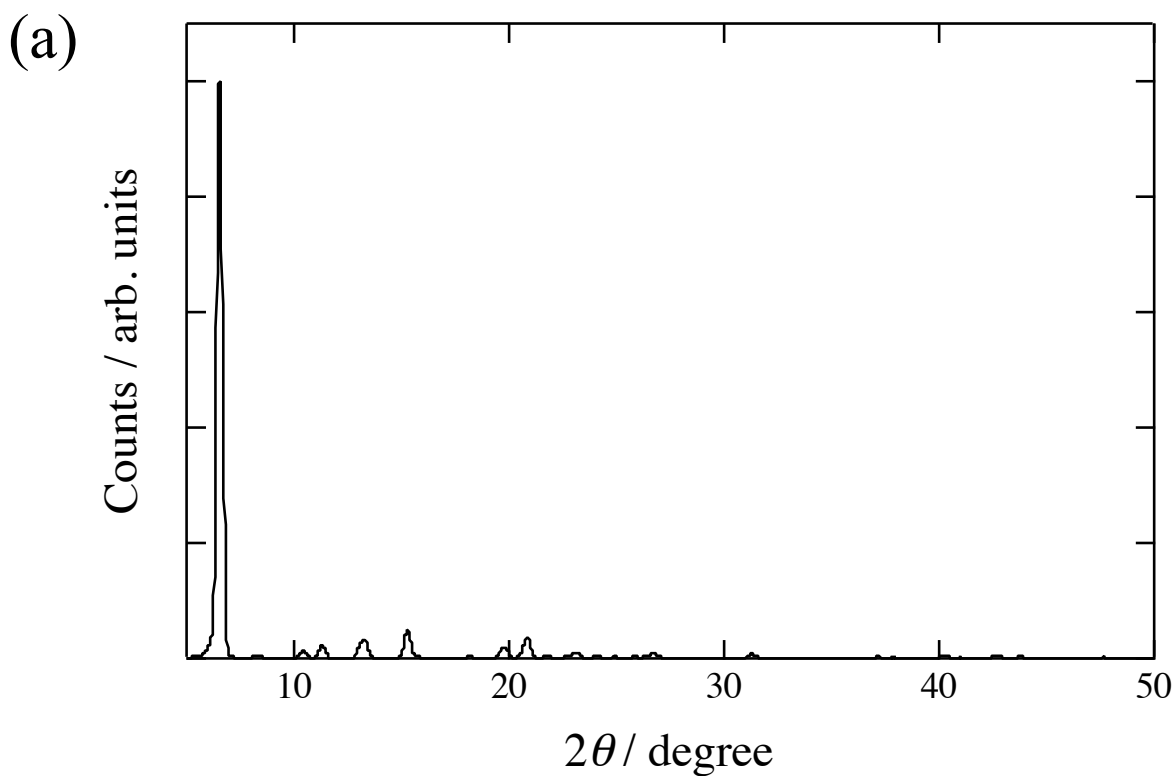
Figure S4. Powder X-ray diffraction patterns of **1** at room temperature (a) and its magnified figure (b).

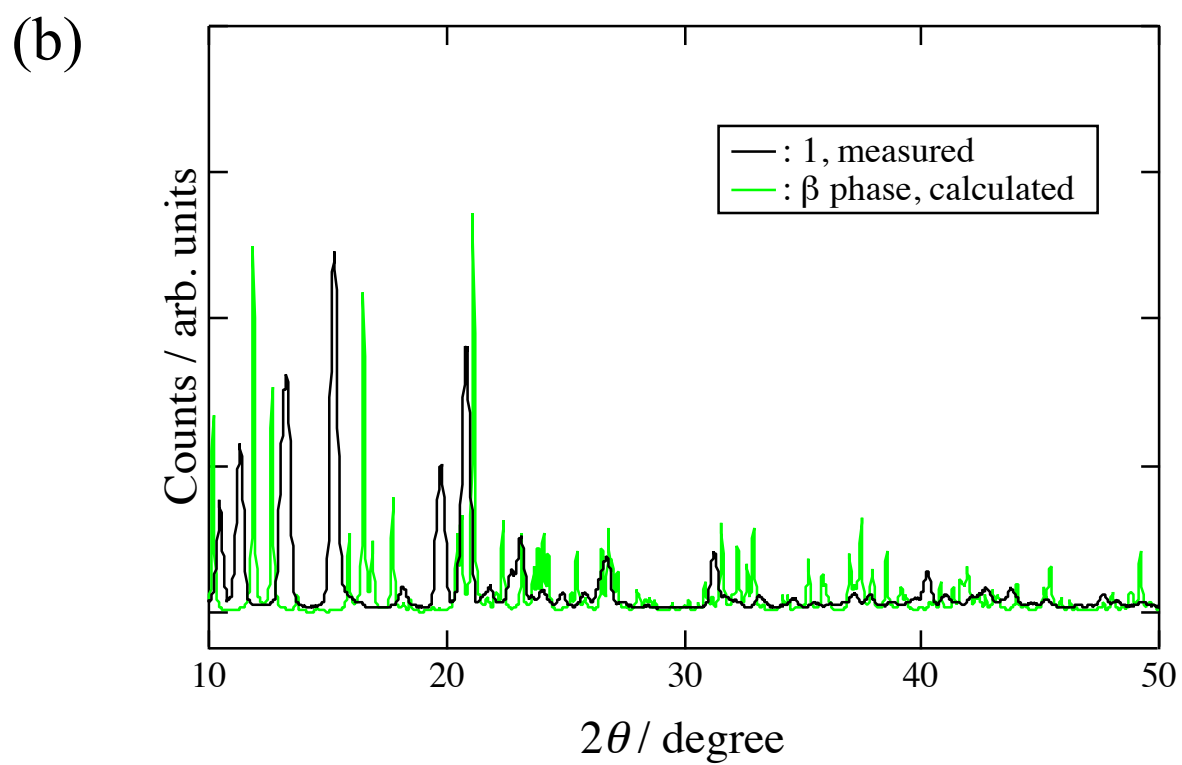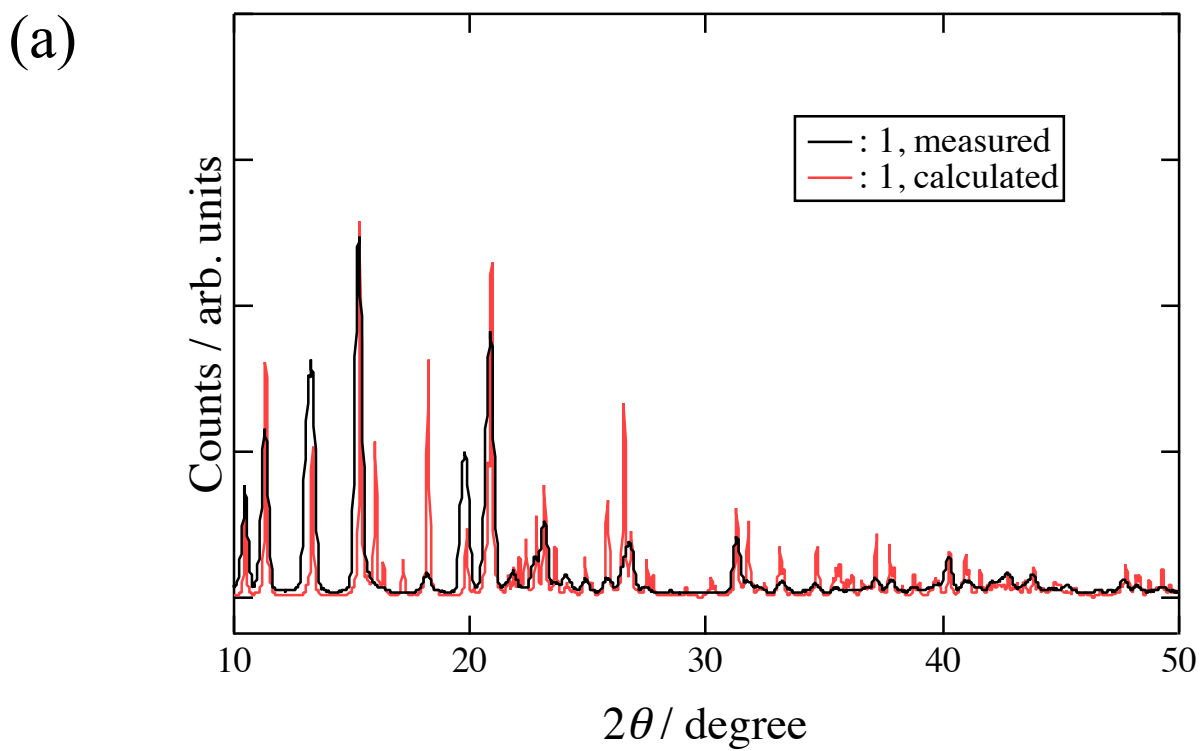The peak of the mark * may be originated to impurity.

Figure S5. Comparison of powder X-ray diffraction patterns of 1 (a) with single crystals of **1** and (b) with single crystals of the β phase.

3. Magnetic Measurements of 1

Magnetic measurements of **1** were carried out for a microcrystalline sample with random orientation on a SQUID (Quantum Design MPMS XL) magnetometer down to 2 K. Temperature dependence of the dc susceptibility was measured under 500 Oe. The molar unit of the paramagnetic susceptibility χ_p was chosen as the quantity per one mole of Cu(II). The experimental raw data were corrected for the diamagnetic contribution, -0.0000903 emu mol^{-1}, which was estimated using Pascal's constants. Field dependence of the magnetization of **1** was carried out at 2 K.
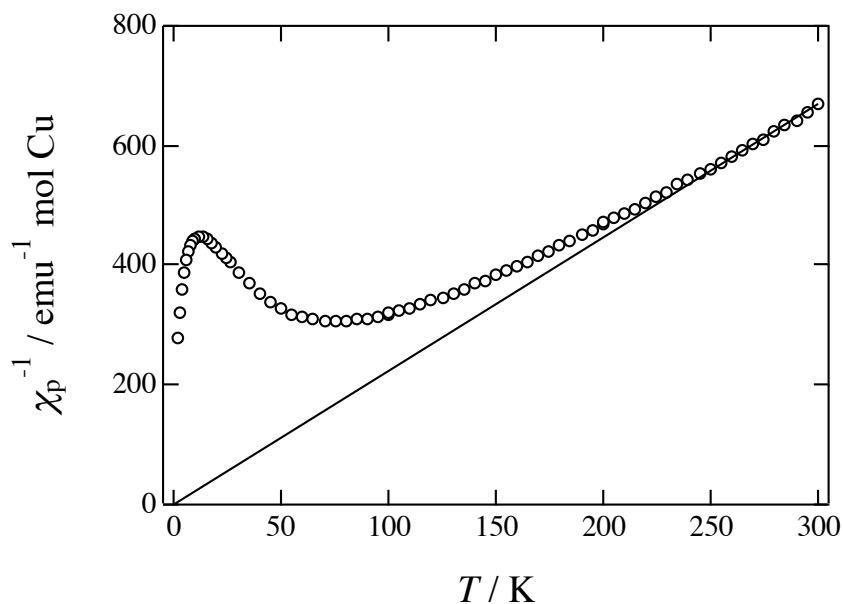
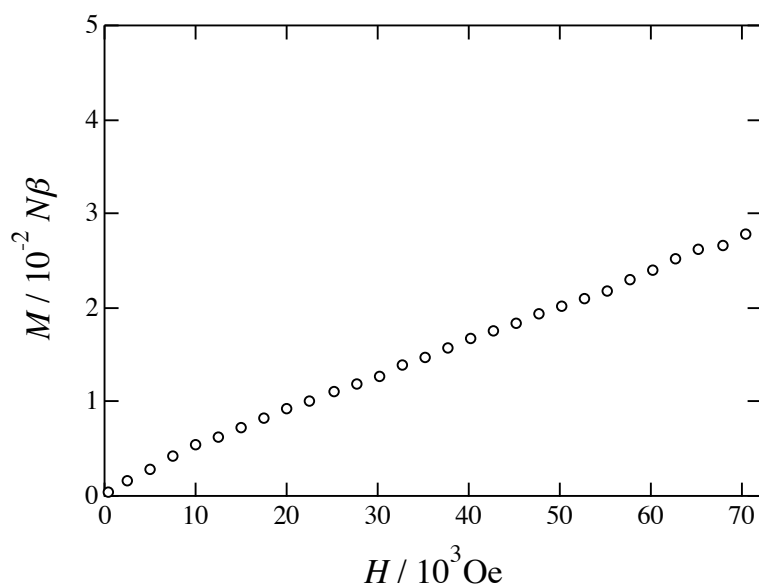Figure S6. Temperature dependence of $1/\chi_p$ for **1** under the dc magnetic field of 500 Oe.

Figure S7. Field dependence of the magnetization for **1** at 2 K.

4. Hamiltonian of a Distorted Diamond Chain Lattice

The Hamiltonian of a distorted diamond chain lattice was defined as follows:[3]

$$H = J_1 \sum_j \left\{ \left(S_{3j-1} \cdot S_{3j} \right)_\Delta + \left(S_{3j} \cdot S_{3j+1} \right)_\Delta \right\} + J_2 \sum_j \left\{ \left(S_{3j+1} \cdot S_{3j+2} \right)_\Delta \right\}$$

$$+ J_3 \sum_j \left\{ \left(S_{3j-2} \cdot S_{3j} \right)_\Delta + \left(S_{3j} \cdot S_{3j+2} \right)_\Delta \right\}$$

where $\left(S_m \cdot S_n \right)_\Delta \equiv S_m^x S_n^x + S_m^y S_n^y + \Delta S_m^z S_n^z$. The parameter Δ is called the interaction anisotropy parameter.

5. 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.

3. K. Okamoto, A. Tokuno and T. Sakai, *J. Mag. Mag. Mater.*, 2007, **310**, e457.