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Electronic Supplementary Information

Magnetically Isolated Cuprate Spin Ladders: Synthesis, Structures, and Magnetic Properties

Xiao Zhang,[a] Sadafumi Nishihara,*[a,b] Yuki Nakano,[a] Erina Yoshida,[a] Chisato Kato,[a] Xiao-Ming Ren,[c] Kseniya Yu. Maryunina,[a] Katsuya Inoue*[a,b]

[a] Department of Chemistry, Hiroshima University, Higashi-hiroshima 739-8526, Japan

[b] Institute for Advanced Materials Research, Hiroshima University, Higashi-hiroshima 739-8530, Japan

[c] College of Science, Nanjing University of Technology, Nanjing 210009, P. R. China, and State Key Lab & Coordination Chemistry Institute, Nanjing University, Nanjing 210093, P. R. China.

Table S1. Select bond lengths (Å) and angles (degrees) for the crystal structure of $Cu_2(CO_3)(ClO_4)_2(NH_3)_6$ (**1**).

Bond lengths (Å)

Cu1(a) – O5(a) Cu1(c) – O5(b)	Cu1(b) – O5(a) Cu1(d) – O5(b)	2.001(5)
Cu1(a) – O6(a)	Cu1(b) – O6(b)	2.833(7)
Cu1(a) – O6(c) Cu1(c) – O6(a)	Cu1(b) – O6(d) Cu1(d) – O6(b)	2.149(7)
Cu1(a) – N1(a) Cu1(c) – N1(c)	Cu1(b) – N1(b) Cu1(d) – N1(d)	2.016(7)
Cu1(a) – N2(a) Cu1(c) – N2(c)	Cu1(b) – N2(b) Cu1(d) – N2(d)	2.021(7)
Cu1(a) – N3(a) Cu1(c) – N3(c)	Cu1(b) – N3(b) Cu1(d) – N3(d)	2.025(8)
C1(a) – O5(a)		1.544(10)
C1(a) – O6(a) C1(b) – O6(c)	C1(a) – O6(b) C1(b) – O6(d)	1.193(7)

Bond angles (degrees)

Cu1(a) – O5(a) – Cu1(b)	Cu1(c) – O5(b) – Cu1(d)	129.6(5)
Cu1(a) – O6(a) – Cu1(c)	Cu1(b) – O6(b) – Cu1(d)	148.0(3)
O5(a) – Cu1(a) – O6(c) O5(b) – Cu1(c) – O6(a)	O5(a) – Cu1(b) – O6(d) O5(b) – Cu1(d) – O6(b)	97.0(3)
O5(a) – Cu1(a) – O6(a)	O5(a) – Cu1(b) – O6(b)	51.1(3)
O6(a) – Cu1(a) – O6(c)	O6(b) – Cu1(b) – O6(d)	148.0(3)
O5(a) – Cu1(a) – N1(a) O5(b) – Cu1(c) – N1(c)	O5(a) – Cu1(b) – N1(b) O5(b) – Cu1(d) – N1(d)	90.14(19)

O5(a) – Cu1(a) – N2(a) O5(b) – Cu1(c) – N2(c)	O5(a) – Cu1(b) – N2(b) O5(b) – Cu1(d) – N2(d)	92.5(2)
O5(a) – Cu1(a) – N3(a) O5(b) – Cu1(c) – N3(c)	O5(a) – Cu1(b) – N3(b) O5(b) – Cu1(d) – N3(d)	167.6(4)
O6(a) – Cu1(a) – N1(a)	O6(b) – Cu1(b) – N1(b)	90.47(18)
O6(a) – Cu1(a) – N2(a)	O6(b) – Cu1(b) – N2(b)	90.23(17)
O6(a) – Cu1(a) – N3(a)	O6(b) – Cu1(b) – N3(b)	116.7(4)
O6(a) – Cu1(c) – N1(c) O6(c) – Cu1(a) – N1(a)	O6(b) – Cu1(d) – N1(d) O6(d) – Cu1(b) – N1(b)	90.6(2)
O6(a) – Cu1(c) – N2(c) O6(c) – Cu1(a) – N2(a)	O6(b) – Cu1(d) – N2(d) O6(d) – Cu1(b) – N2(b)	90.3(2)
O6(a) – Cu1(c) – N3(c) O6(c) – Cu1(a) – N3(a)	O6(b) – Cu1(d) – N3(d) O6(d) – Cu1(b) – N3(b)	95.3(4)
N1(a) – Cu1(a) – N2(a) N1(c) – Cu1(c) – N2(c)	N1(b) – Cu1(b) – N2(b) N1(d) – Cu1(d) – N2(d)	177.1(3)
N1(a) – Cu1(a) – N3(a) N1(c) – Cu1(c) – N3(c)	N1(b) – Cu1(b) – N3(b) N1(d) – Cu1(d) – N3(d)	88.4(3)
N2(a) – Cu1(a) – N3(a) N2(c) – Cu1(c) – N3(c)	N2(b) – Cu1(b) – N3(b) N2(d) – Cu1(d) – N3(d)	88.8(3)
O5(a) – C1(a) – O6(a)		107.4(3)
O5(a) – C1(a) – O6(b)		107.4(3)
O6(a) – C1(a) – O6(b)	O6(c) – C1(b) – O6(d)	145.3(7)

Table S2. Select bond lengths (Å) and angles (degrees) for the crystal structure of $Cu_2(CO_3)(ClO_4)_2(H_2O)(NH_3)_5$ (**2**) at 100 K (LT phase).

Bond lengths (Å)

Cu2(a) – O3(a)	Cu2(b) – O3(b)	2.221(3)
Cu2(a) – O1(b)	Cu2(b) – O1(a)	1.946(3)
Cu1(a) – O3(a)	Cu1(b) – O3(b)	2.003(3)
Cu1(a) – O2(b)	Cu1(b) – O2(a)	2.324(3)
Cu1(a) – O1(a)		2.622
Cu2(a) – O6(a)	Cu2(b) – O6(b)	2.056(3)
Cu2(a) – N1(a)	Cu2(b) – N1(b)	1.991(3)
Cu1(a) – N2(a)	Cu1(b) – N2(b)	2.005(3)
Cu1(a) – N3(a)	Cu1(b) – N3(b)	2.034(4)
C1(a) – O3(a)		1.291(5)
C1(a) – O1(a)	C1(b) – O1(b)	1.287(5)
C1(a) – O2(a)	C1(b) – O2(b)	1.267(5)

Bond angles (degrees)

Cu2(a) – O3(a) – Cu1(a)	Cu2(b) – O3(b) – Cu1(b)	123.18(13)
Cu1(a) – O1(a) – Cu2(b)		151.57
O3(a) – Cu2(a) – O1(b)	O3(b) – Cu2(b) – O1(a)	108.48(11)
O3(a) – Cu1(a) – O2(b)	O3(b) – Cu1(b) – O2(a)	89.24(11)
O3(a) – Cu1(a) – O1(a)		54.51
O3(a) – Cu2(a) – N1(a)	O3(b) – Cu2(b) – N1(b)	93.15(8)
O3(a) – Cu2(a) – O6(a)	O3(b) – Cu2(b) – O6(b)	90.49(11)
O3(a) – Cu1(a) – N2(a)	O3(b) – Cu1(b) – N2(b)	89.86(7)

O3(a) – Cu1(a) – N3(a)	O3(b) – Cu1(b) – N3(b)	167.65(14)
O1(b) – Cu2(a) – N1(a)	O1(a) – Cu2(b) – N1(b)	90.59(8)
O1(b) – Cu2(a) – O6(a)	O1(a) – Cu2(b) – O6(b)	161.03(13)
O2(b) – Cu1(a) – N2(a)	O2(a) – Cu1(b) – N2(b)	89.03(8)
O2(b) – Cu1(a) – N3(a)	O2(a) – Cu1(b) – N3(b)	103.11(13)
O2(b) – Cu1(a) – O1(a)		151.57
N1(a) – Cu2(a) – N1(a)	N1(b) – Cu2(b) – N1(b)	172.86(16)
N2(a) – Cu1(a) – N2(a)	N2(b) – Cu1(b) – N2(b)	178.04(15)
N1(a) – Cu2(a) – O6(a)	N1(b) – Cu2(b) – O6(b)	88.30(8)
N2(a) – Cu1(a) – N3(a)	N2(b) – Cu1(b) – N3(b)	90.34(7)
O3(a) – C1(a) – O2(a)		120.6(4)
O3(a) – C1(a) – O1(a)		116.1(4)
O2(a) – C1(a) – O1(a)	O2(b) – C1(b) – O1(b)	123.3(4)

Table S3. Select bond lengths (Å) and angles (degrees) for the crystal structure of $Cu_2(CO_3)(ClO_4)_2(H_2O)(NH_3)_5$ (**2**) at room temperature (HT phase).

Bond lengths (Å)

Cu2(a) – O3(a)	Cu2(b) – O3(b)	2.259(3)
Cu2(a) – O1(b)	Cu2(b) – O1(a)	1.950(3)
Cu1(a) – O3(a)	Cu1(b) – O3(b)	2.001(3)
Cu1(a) – O2(b)	Cu1(b) – O2(a)	2.373(3)
Cu1(a) – O1(a)		2.630
Cu2(a) – O6(a)	Cu2(b) – O6(b)	2.053(3)
Cu2(a) – N1(a)	Cu2(b) – N1(b)	1.986(3)
Cu1(a) – N2(a)	Cu1(b) – N2(b)	2.005(3)
Cu1(a) – N3(a)	Cu1(b) – N3(b)	2.035(4)
C1(a) – O3(a)		1.294(5)
C1(a) – O1(a)	C1(b) – O1(b)	1.281(5)
C1(a) – O2(a)	C1(b) – O2(b)	1.257(5)

Bond angles (degrees)

Cu2(a) – O3(a) – Cu1(a)	Cu2(b) – O3(b) – Cu1(b)	122.46(12)
Cu1(a) – O1(a) – Cu2(b)		152.80
O3(a) – Cu2(a) – O1(b)	O3(b) – Cu2(b) – O1(a)	109.79(12)
O3(a) – Cu1(a) – O2(b)	O3(b) – Cu1(b) – O2(a)	88.55(10)
O3(a) – Cu1(a) – O1(a)		54.19
O3(a) – Cu2(a) – N1(a)	O3(b) – Cu2(b) – N1(b)	93.85(9)
O3(a) – Cu2(a) – O6(a)	O3(b) – Cu2(b) – O6(b)	88.82(12)

O3(a) – Cu1(a) – N2(a)	O3(b) – Cu1(b) – N2(b)	90.22(8)
O3(a) – Cu1(a) – N3(a)	O3(b) – Cu1(b) – N3(b)	168.01(15)
O1(b) – Cu2(a) – N1(a)	O1(a) – Cu2(b) – N1(b)	90.51(9)
O1(b) – Cu2(a) – O6(a)	O1(a) – Cu2(b) – O6(b)	161.39(14)
O2(b) – Cu1(a) – N2(a)	O2(a) – Cu1(b) – N2(b)	88.64(8)
O2(b) – Cu1(a) – N3(a)	O2(a) – Cu1(b) – N3(b)	103.44(15)
O2(b) – Cu1(a) – O1(a)		142.75
N1(a) – Cu2(a) – N1(a)	N1(b) – Cu2(b) – N1(b)	171.38(18)
N2(a) – Cu1(a) – N2(a)	N2(b) – Cu1(b) – N2(b)	177.24(16)
N1(a) – Cu2(a) – O6(a)	N1(b) – Cu2(b) – O6(b)	88.15(9)
N2(a) – Cu1(a) – N3(a)	N2(b) – Cu1(b) – N3(b)	90.07(8)
O3(a) – C1(a) – O2(a)		120.6(4)
O3(a) – C1(a) – O1(a)		115.9(4)
O2(a) – C1(a) – O1(a)	O2(b) – C1(b) – O1(b)	123.5(4)

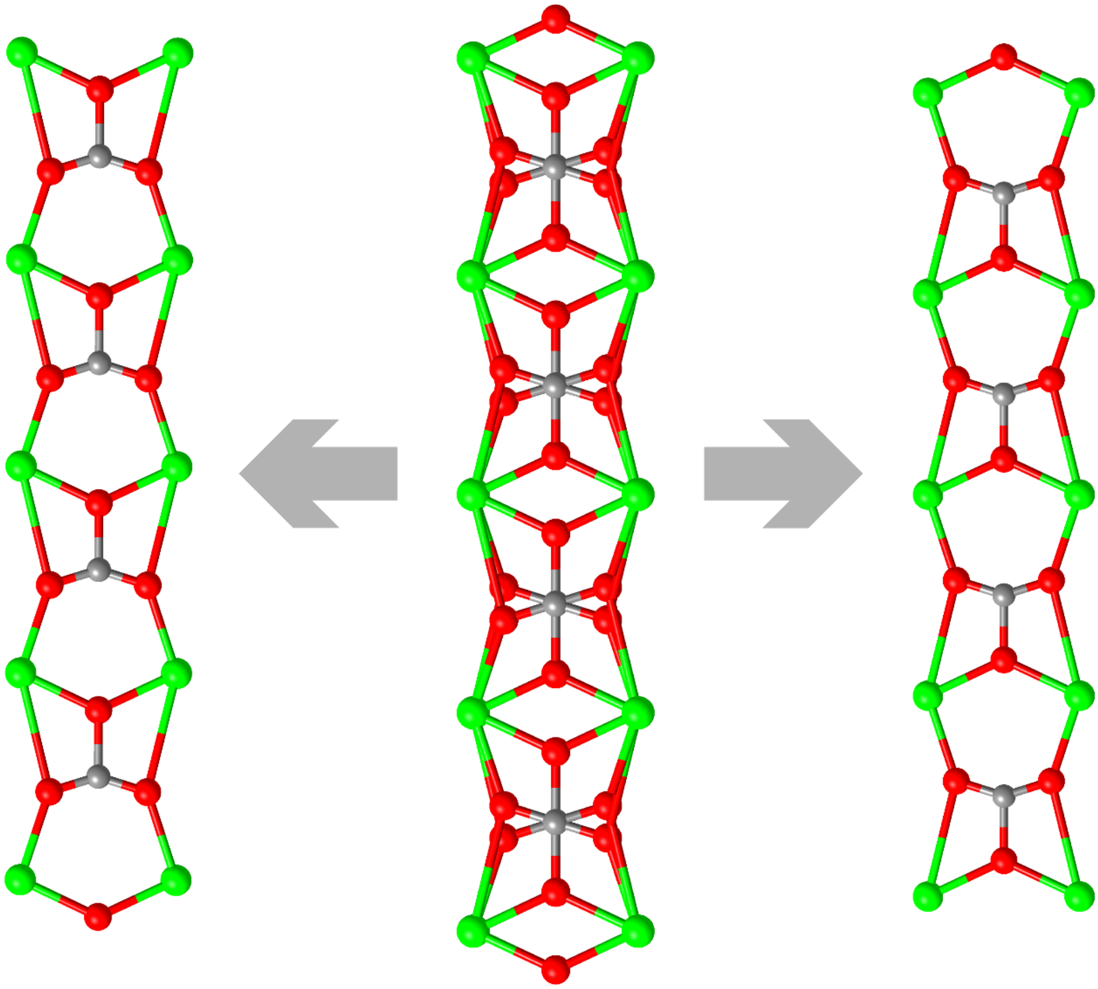

Figure S1. Schematic splitting of the disordered ladder configuration of $Cu_2(CO_3)(ClO_4)_2(NH_3)_6$ (**1**) into two antiparallel crystallographically equivalent ladders.

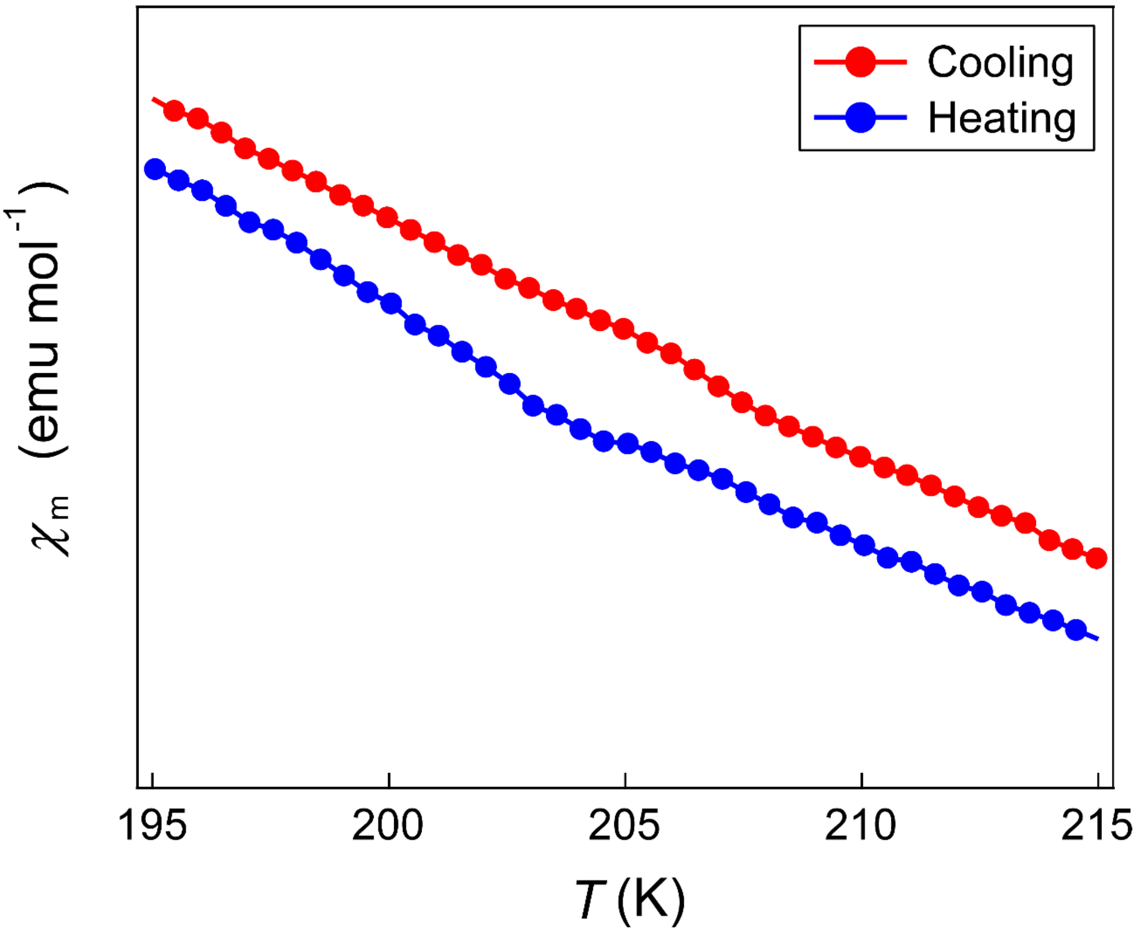

Figure S2. Variation in the molar susceptibility of $Cu_2(CO_3)(ClO_4)_2(H_2O)(NH_3)_5$ (**2**) with increasing (blue) and decreasing (red) temperature in the 195 - 215 K range.

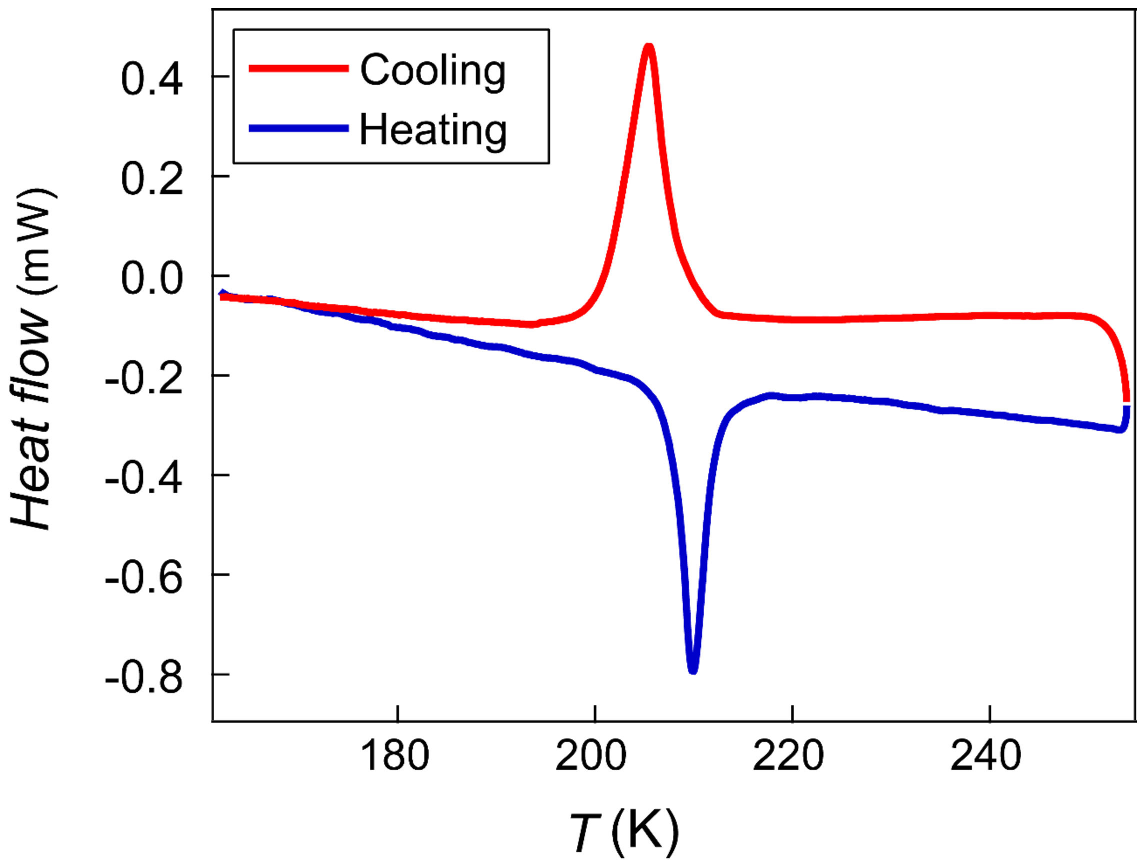

Figure S3. DSC curve for $Cu_2(CO_3)(ClO_4)_2(H_2O)(NH_3)_5$ (**2**).

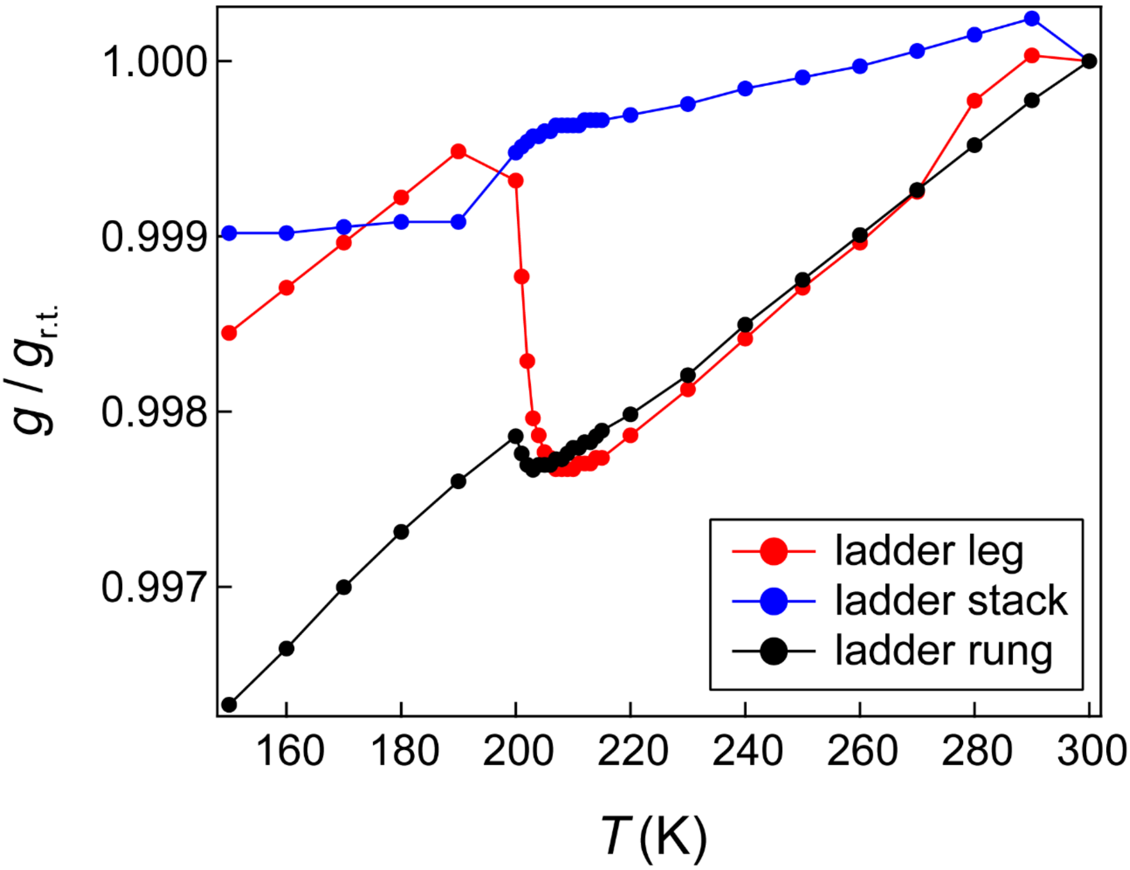

Figure S4. Temperature-dependent g / $g_{r.t.}$ for $Cu_2(CO_3)(ClO_4)_2(H_2O)(NH_3)_5$ (**2**), where g values are estimated by ESR measurement.

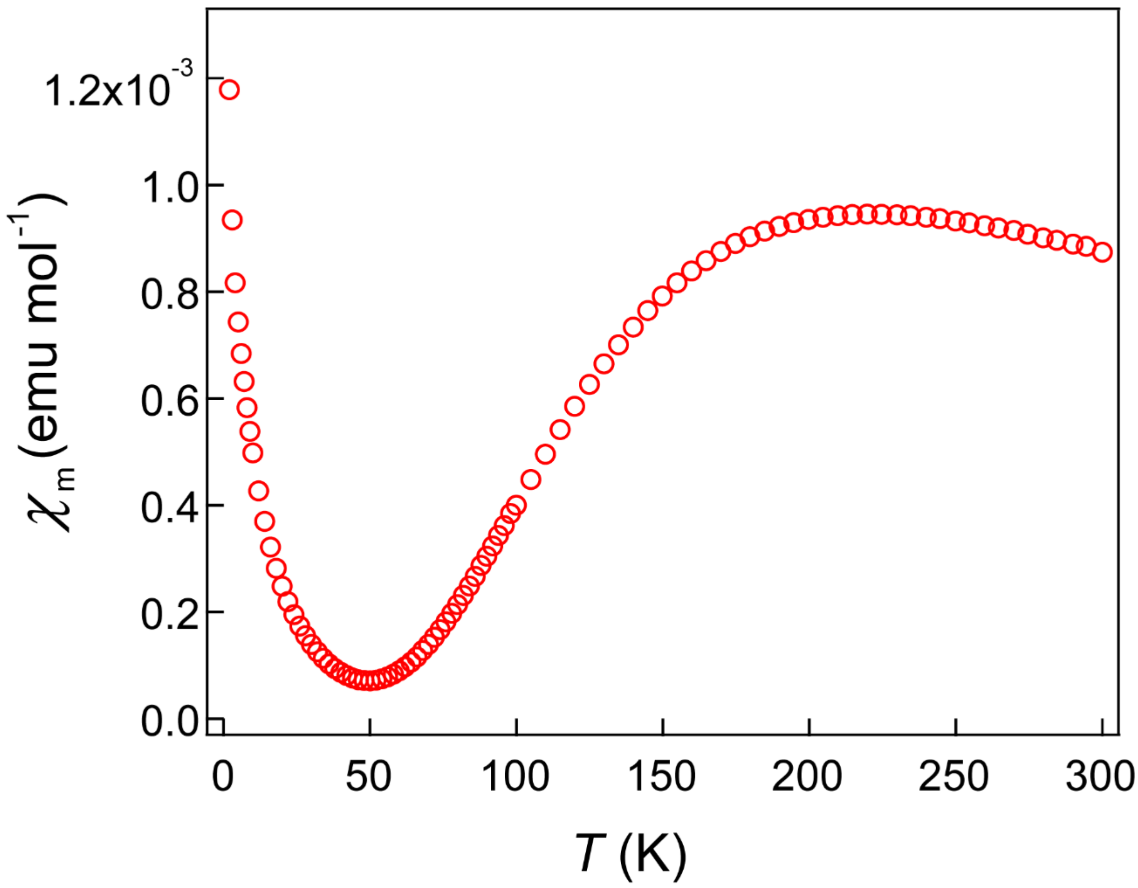

Figure S5. Temperature-dependent molar magnetic susceptibility of $Cu_2(CO_3)(ClO_4)_2(NH_3)_6$ (**1**).

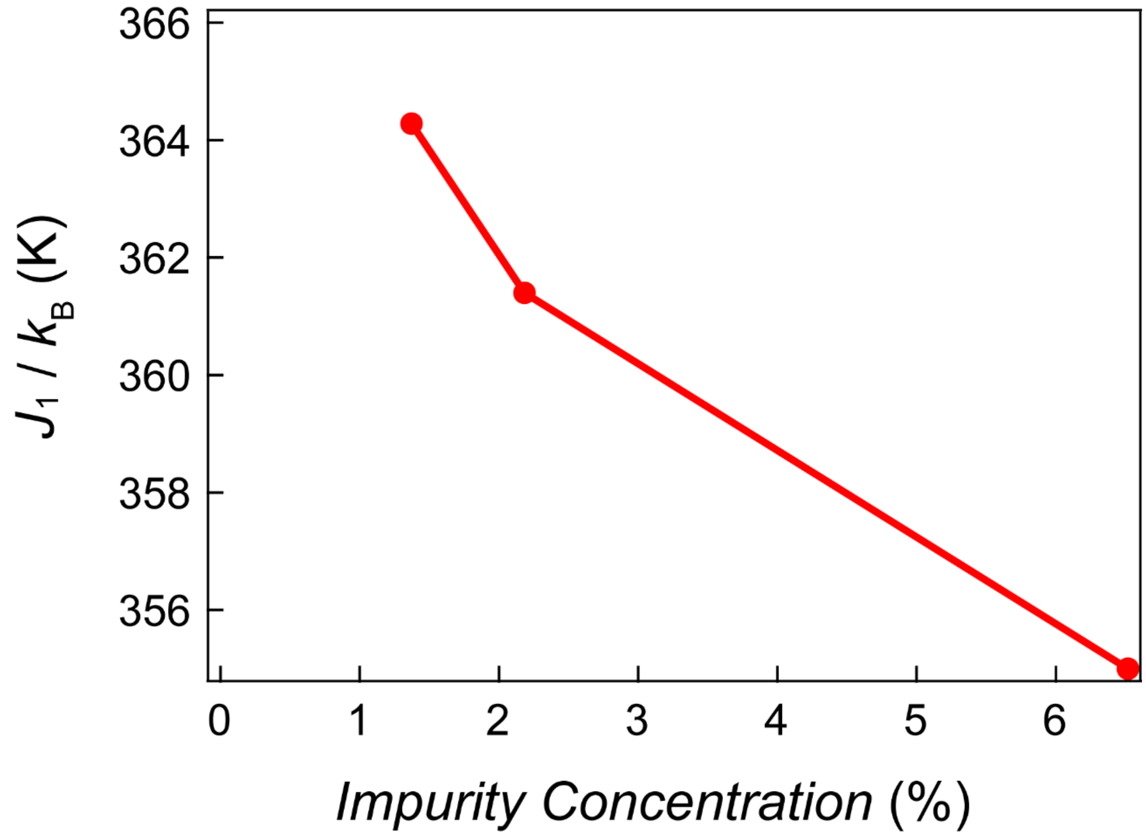

Figure S6. The ladder-rung interaction J_1 plotted against impurity concentration, which were estimated by magnetic susceptibility measurements of $Cu_2(CO_3)(ClO_4)_2(NH_3)_6$ (**1**).

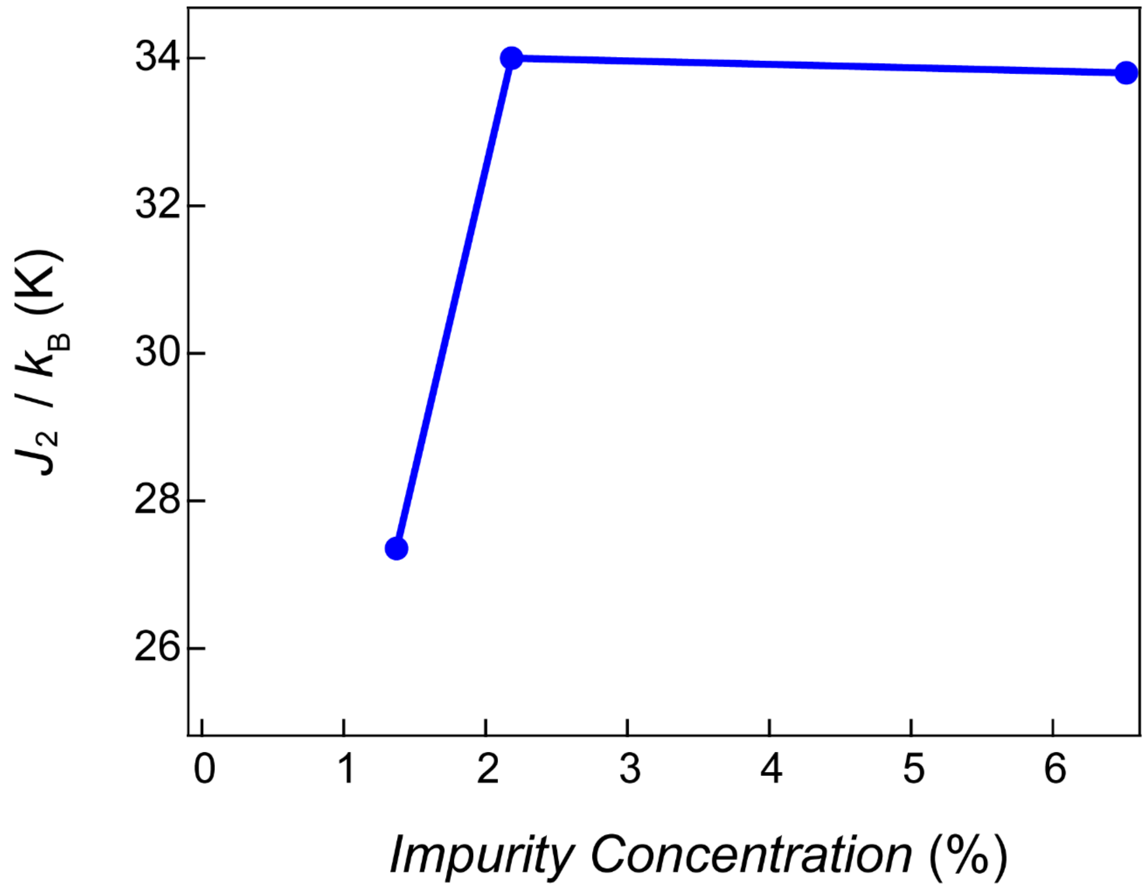

Figure S7. The ladder-leg interaction J_2 plotted against impurity concentration, which were estimated by magnetic susceptibility measurements of $Cu_2(CO_3)(ClO_4)_2(NH_3)_6$ (**1**).

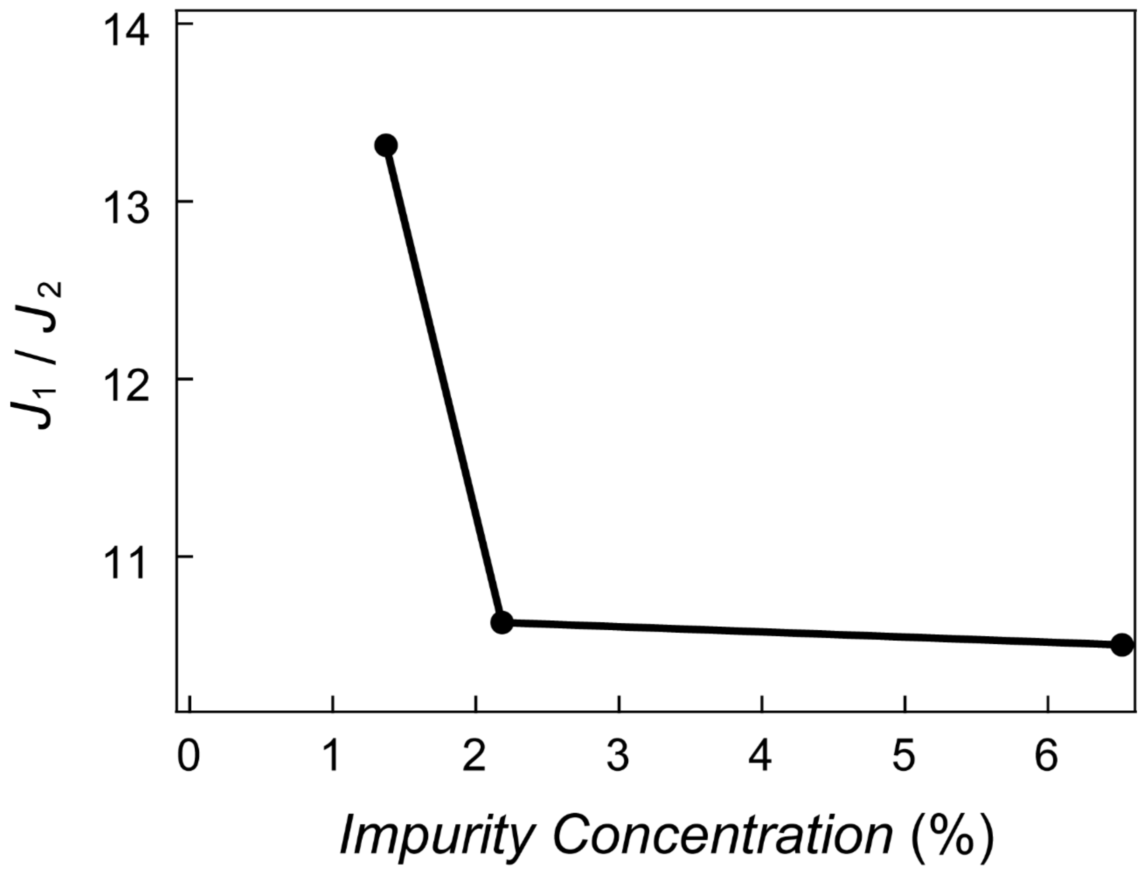

Figure S8. The ration of ladder-rung interaction J_1 to ladder-leg interaction J_2 plotted against impurity concentration, which were estimated by magnetic susceptibility measurements of $Cu_2(CO_3)(ClO_4)_2(NH_3)_6$ (**1**).

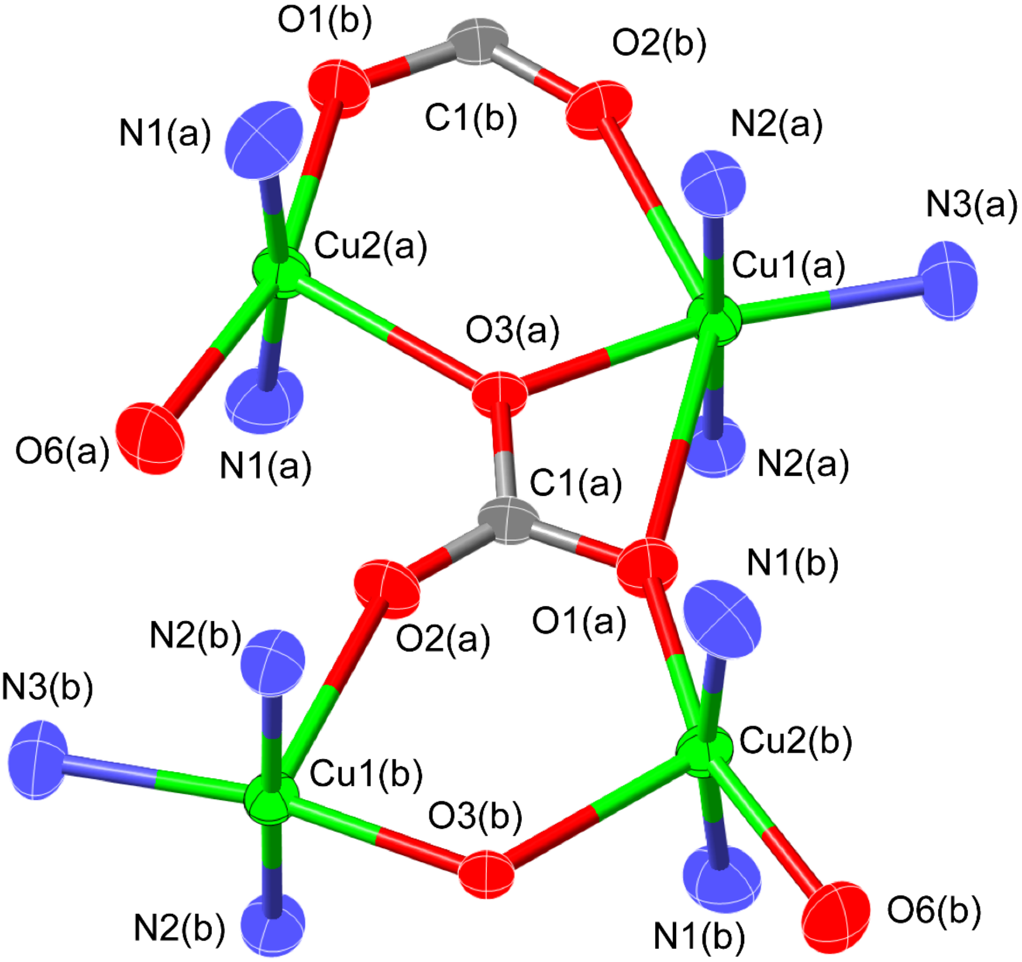

Figure S9. Thermal ellipsoid plot (50% probability level) of the partial structure of $Cu_2(CO_3)(ClO_4)_2(H_2O)(NH_3)_5$ (**2**) at room temperature, along with the atom numbering scheme.

Equation 1 S = 1/2 magnetically isolated spin-ladder model

$$\chi = \frac{Ng^2\beta^2 e^{-\Delta^*_{fit}/t}}{J_1 \quad 4t} P^{(p)}_{(q)}(t)$$

$$t \equiv \frac{k_B T}{J_1}$$

$$P^p_q = \frac{1 + \sum_{n=1}^{p} N_n / t^n}{1 + \sum_{n=1}^{q} D_n / t^n}$$

where the parameters Δ_{fit}^*, N_{n}, D_{n} are described in Appendix 5 of Ref .45

Equation 2 Alternating chain model

$$\chi = \frac{Ng^2\beta^2}{kT} \frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3}$$

$x = |J| \;/\; k_B T$

A = 0.25

B = (-0.068475 + (0.13194*α))

C = (0.0042563 - (0.031670*α) + (0.12278*(α^2)) - (0.29943*(α^3)) + (0.21814*(α^4)))

D = (0.035255 + (0.65210*α))

E = (-0.00089418 - (0.10209*α) + (0.87155*(α^2)) - (0.18472*(α^3)))

F = (0.045230 - (0.0081910*α) + (0.83234*(α^2)) - (2.6181*(α^3)) + (1.92813*(α^4)))