Supporting Information for

Spin dynamics in a Heisenberg weak antiferromagnetic chain of an iodide-bridged Cu(II) complex

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Methods

Materials. CuI, dehydrated ethanol (EtOH), and 2-propanol (2-PrOH) were purchased from Fujifilm Wako Pure Chemical Corp. 1*R*,2*R*-diaminocyclohexane (chxn) was purchased from Sigma-Aldrich.

Synthesis of [$Cu^{II}(chxn)_2I$]I. Refluxing CuI (300 mg, 1.6 mmol), chxn (580 mg, 5.1 mmol), and I (200 mg, 1.6 mmol) in EtOH (60 mL) for 1 h afforded a blue-purple solution. Following hot filtration, blue-purple needle-like crystals appeared after leaving the capped solution to stand for 3 days. The compound was obtained in a 65% yield by filtration and rapidly washing with EtOH (3 × 5 mL) and 2-PrOH (3 × 5 mL) and drying *in vacuo* overnight at room temperature. Elemental analysis calcd (%) for $C_{12}H_{28}N_4CuI_2$ ([$Cu^{II}(chxn)_2I$]I): C 26.41, H 5.17, N 10.27; found: C 26.13, H 5.42, N 10.16.

Measurements. The elemental analysis was performed using a J-Science Lab Co. Ltd. JM11 at the Research and Analytical Center for Giant Molecules (Tohoku Univ.). PXRD measurements were carried out with Cu-Kα radiation using a Rigaku Ultima IV diffractometer at room temperature. Magnetic measurements were performed using a magnetic property measurement system (MPMS-XL, Quantum Design) in both DC mode and AC mode. The sample was placed into a gelatin capsule (Matsuya) which was fixed in a plastic straw. ESR spectrum was recorded on a JEOL JES-X330 at X-band at room temperature.

Collection of crystallographic data and structure refinements. A suitable single crystal of [$Cu^{II}(chxn)_2I$]I was selected and mounted onto a MicroMount (MiTeGen) in an XtaLAB AFC10 diffractometer with a HyPix-6000HE hybrid pixel array detector. The crystal was kept at 120 K during data collection using a N_2 flow-type temperature controller. Using Olex2,[S1] the structure was solved with the SHELXT[S2] structure solution program, using intrinsic phasing, and refined with the SHELXL[S3] refinement package using least-squares minimization. The X-ray crystallographic coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC-2243196).

Quantum chemical calculations

DFT calculations of the singlet and the triplet states of a dimer model, $[Cu^{II}_2(chxn)_4I_3]^+$, were performed at an unrestricted UB3LYP/SDD level of theory. All calculations were performed using the Gaussian 16W package.[33,34] The atomic coordinates used were those of the crystal structure without alteration (Table S2). Calculation of the coupling constant was performed using the Heisenberg model and size-consistent spin projection (Table S3).[S4]

Table S1. Crystallographic data for $[Cu^{II}(chxn)_2I]I$

Formula	$C_{12}H_{28}CuI_2N_4$
Formula weight	545.72
Crystal size (mm^3)	0.20 × 0.05 × 0.05
Crystal system	Trigonal
Space group	$P3_221$
a (Å)	9.3636(2)
b (Å)	9.3636(2)
c (Å)	18.1008(3)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	1374.40(6)
T (K)	120
Z	3
D_{calc} (g cm^{-3})	1.978
F (000)	789.0
λ (Mo Kα) (Å)	0.71073
μ (mm^{-1})	4.556
Reflections collected	24499
Data/restraints/parameters	2940/0/89
GOF on F^2	1.060
R_{int}	0.0349
$R_1{}^a$	0.0132
$wR_2{}^b$ (all data)	0.0320

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$.

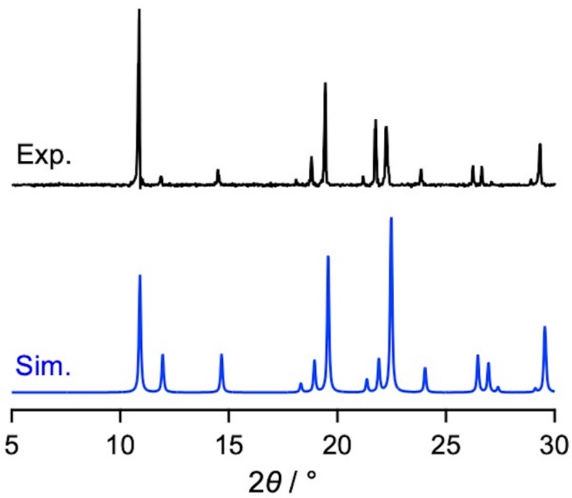

Figure S1. PXRD of [$Cu^{II}(chxn)_2I$]I together with that of a simulation.

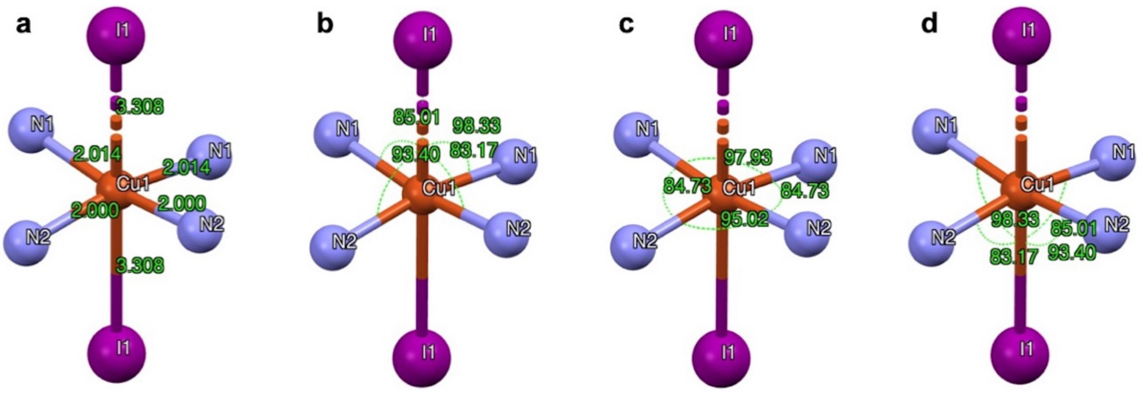

Figure S2. (a) Bond lengths (Å) and (b–d) angles (°) around the Cu(II) center in [$Cu^{II}(chxn)_2I$]I.

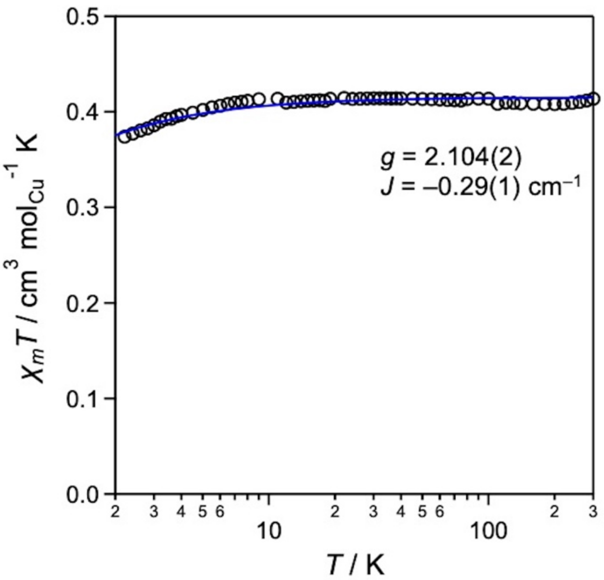

Figure S3. (a) The log-scale $\chi_m T$–T plot of $[Cu^{II}(chxn)_2I]I$ with a fitting curve (blue line).

Table S2. Cartesian coordinates of $[Cu^{II}(chxn)_2I]I$

Number	Atom	*x* (Å)	*y* (Å)	*z* (Å)
1	53	-0.000002	1.338592	-0.000007
2	29	-3.061092	0.096401	0.177803
3	7	-2.524748	-0.322339	2.058441
4	1	-1.735963	0.088594	2.250674
5	1	-3.155866	-0.008276	2.633995
6	7	-2.614156	-1.833584	-0.1828
7	1	-3.378648	-2.321771	-0.254998
8	1	-2.1531	-1.905354	-0.964079
9	6	-1.511124	-2.170698	3.417835
10	1	-1.911966	-1.818443	4.252039
11	1	-0.610828	-1.771442	3.316416
12	6	-2.378596	-1.782553	2.23071
13	1	-3.287837	-2.177929	2.361583
14	6	-1.7906	-2.34252	0.941708
15	1	-0.866699	-1.973835	0.838392
16	6	-0.843737	-4.28639	2.219354
17	1	-0.843479	-5.274029	2.288856
18	1	0.091311	-3.988381	2.089178
19	6	-1.685524	-3.861785	1.014166
20	1	-1.270421	-4.204522	0.182803
21	1	-2.591773	-4.252934	1.088504
22	6	-1.391939	-3.687649	3.507544
23	1	-0.792438	-3.924562	4.259219
24	1	-2.283425	-4.075168	3.695001
25	7	-3.881749	1.865935	0.619484
26	1	-4.731088	1.7427	0.92187
27	1	-3.401796	2.270067	1.278672
28	7	-3.229776	0.704393	-1.7344
29	1	-2.417779	0.966881	-2.05023
30	1	-3.531711	0.020167	-2.25285
31	6	-4.924356	3.851993	-0.503174
32	1	-4.720394	4.435132	0.270778
33	1	-5.828377	3.470436	-0.371324
34	6	-3.902161	2.728751	-0.579846
35	1	-2.99513	3.134627	-0.692667
36	6	-4.184985	1.838826	-1.783537
37	1	-5.108529	1.468441	-1.683144
38	6	-5.137468	3.809395	-3.015281
39	1	-5.046358	4.362937	-3.831095
40	1	-6.059614	3.450086	-2.990493
41	6	-4.140959	2.649694	-3.07389
42	1	-4.360381	2.062736	-3.840883
43	1	-3.22707	3.004543	-3.210635
44	6	-4.89749	4.675047	-1.785848
45	1	-5.594779	5.376558	-1.738775
46	1	-4.018886	5.123766	-1.868089
47	53	-6.152933	-0.999691	0.60679
48	29	3.061081	0.096393	-0.177714
49	7	2.52475	-0.322308	-2.058446
50	1	1.735963	0.088559	-2.250677

Table S2. Cartesian coordinates of [Cu^{II}($chxn)_2$I]I (continue)

Number	Atom	*x* (Å)	*y* (Å)	*z* (Å)
51	1	3.155864	-0.008204	-2.633979
52	7	2.614167	-1.833622	0.182763
53	1	3.378656	-2.321709	0.255001
54	1	2.153104	-1.905348	0.964097
55	6	1.511124	-2.17068	-3.417776
56	1	1.911975	-1.818387	-4.252063
57	1	0.610831	-1.77148	-3.316386
58	6	2.378611	-1.782596	-2.230779
59	1	3.287846	-2.177925	-2.361595
60	6	1.79061	-2.342537	-0.941718
61	1	0.866707	-1.973828	-0.838397
62	6	0.843746	-4.286389	-2.219306
63	1	0.843501	-5.274022	-2.288886
64	1	-0.0913	-3.988355	-2.089153
65	6	1.685536	-3.861732	-1.014151
66	1	1.270437	-4.204554	-0.182813
67	1	2.591791	-4.252915	-1.08853
68	6	1.391959	-3.687538	-3.507602
69	1	0.792449	-3.924578	-4.259191
70	1	2.283438	-4.075131	-3.694997
71	7	3.881739	1.865978	-0.619453
72	1	4.731078	1.742803	-0.921834
73	1	3.401789	2.270113	-1.278679
74	7	3.229773	0.704363	1.734399
75	1	2.417778	0.966906	2.050212
76	1	3.53171	0.020162	2.252861
77	6	4.92434	3.851961	0.503192
78	1	4.720374	4.435193	-0.270741
79	1	5.828361	3.470498	0.371352
80	6	3.902153	2.728836	0.579838
81	1	2.995112	3.13464	0.692731
82	6	4.184971	1.838833	1.783598
83	1	5.108519	1.468463	1.683177
84	6	5.137452	3.809346	3.015306
85	1	5.046335	4.362949	3.831155
86	1	6.059594	3.44999	2.990553
87	6	4.140951	2.649698	3.073879
88	1	4.360366	2.062718	3.840949
89	1	3.227054	3.004558	3.210678
90	6	4.897478	4.675013	1.78581
91	1	5.594752	5.376523	1.738843
92	1	4.018863	5.123768	1.868125
93	53	6.152943	-0.999678	-0.606844

Table S3. Summary of DFT calculation results

State	Open-shell triplet (HS)	Open-shell singlet (LS)
Electronic energy [Hartree]	-1814.63670644	-1814.63670723
$<S^2>$	2.0044	1.0044
$E^{LS} - E^{HS}$ [cm^{-1}]	–0.17	
J [cm^{-1}]	–0.17	

Calculations were performed using UB3LYP/SDD with the Heisenberg model and size-consistent spin projection.[S4]

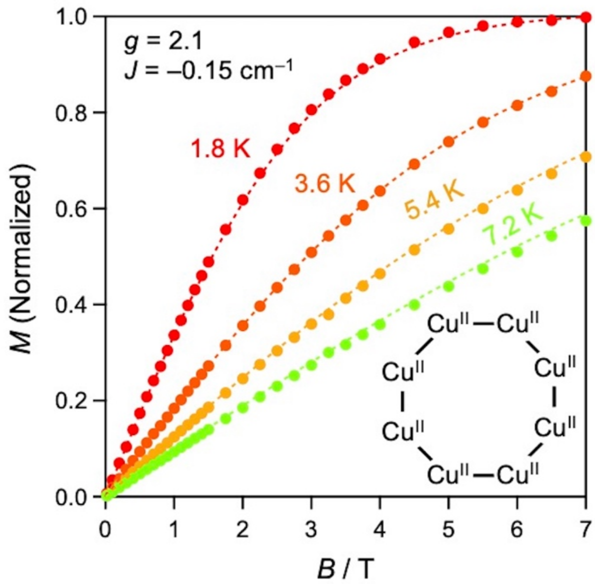

Figure S4. Magnetization-field curves normalized by the saturation magnetization (M_S) at 1.8 K of [$Cu^{II}(chxn)_2I$]I. The temperature dependence was measured at 1.8, 3.6, 5.4, and 7.2 K. Dotted curves show normalized simulation curves of the 8-ring model with g_{iso} = 2.1 and J = –0.15 cm^{-1}, using the program PHI.[S5] Weak antiferromagnetism is confirmed like as the Eggert-Affleck-Takahashi mode (Figure 2).

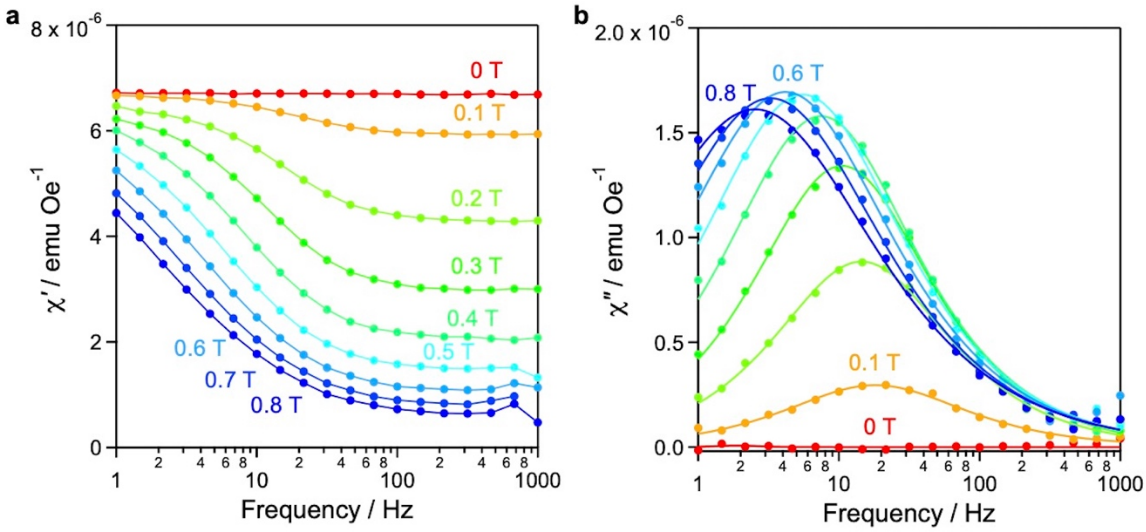

Figure S5. (a) The real part (χ') and (b) the imaginary part (χ'') of AC susceptibility of $[Cu^{II}(chxn)_2I]I$, measured at 1.8 K under a static magnetic field of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 T. AC drive is 2.5 Oe. Each line for χ'' is a Debye relaxation fitting curve.

Table S4. AC susceptibility fitting data of the imaginary part of $[Cu^{II}(chxn)_2I]I$ at 1.8 K

H [Oe]	χ_T-χ_S [emu/Oe]	τ [s]	α	σ χ_T-χ_S [emu/Oe]	σ τ [s]	σ α
0	–	–	–	–	–	–
1000	7.71E-07	0.008784	0.16722	1.67E-08	0.000328	0.0177
2000	2.23E-06	0.011007	0.14547	2.05E-08	0.000169	0.0076
3000	3.42E-06	0.015118	0.15364	2.74E-08	0.000201	0.00661
4000	4.31E-06	0.021319	0.19546	5.34E-08	4.59E-04	0.01
5000	4.87E-06	0.028833	0.22984	6.05E-08	6.50E-04	0.00973
6000	5.17E-06	0.03819	0.26124	1.12E-07	1.59E-03	0.016
7000	5.31E-06	0.04875	0.28695	5.88E-08	1.09E-03	0.00761
8000	5.48E-06	0.062693	0.32286	9.85E-08	0.00251	0.011

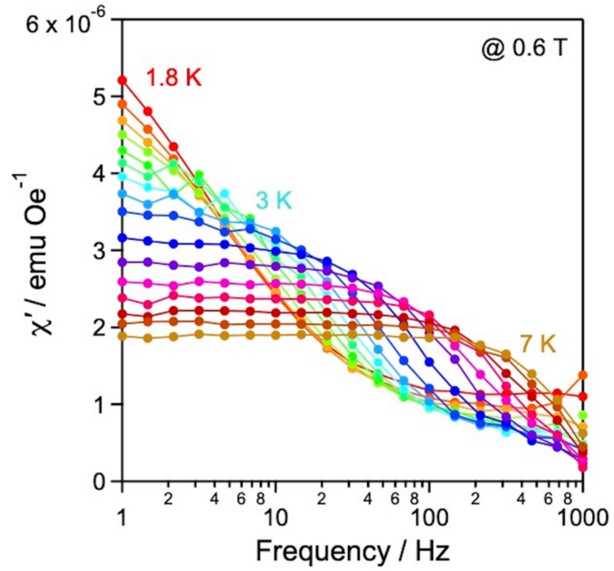

Figure S6. The real part (χ') of AC susceptibility of [Cu^{II}(chxn)$_2$I]I, measured at 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, and 7.0 K under a static magnetic field of 0.6 T. AC drive is 2.5 Oe.

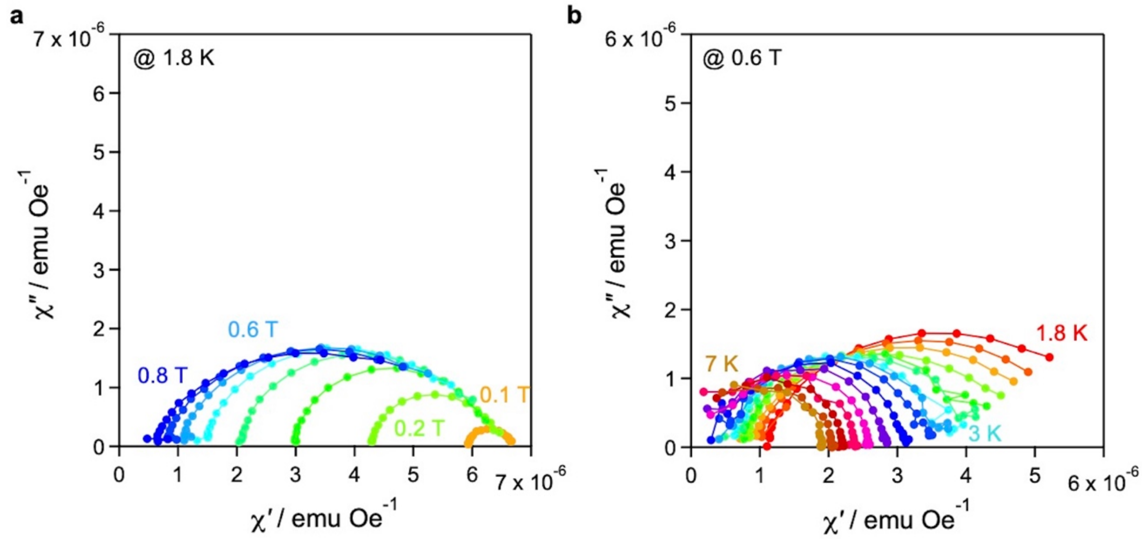

Figure S7. Cole-Cole plots of AC susceptibility of [Cu^{II}(chxn)$_2$I]I, measured at (a) 1.8 K under 0.1, 0.2 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 T; and (b) at 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, and 7.0 K under 0.6 T.

Table S5. AC susceptibility fitting data of the imaginary part of [Cu^{II}(chxn)$_2$I]I

T [K]	χ_T-χ_S [emu/Oe]	τ [s]	α	σ χ_T-χ_S [emu/Oe]	σ τ [s]	σ α
1.8	5.25E-06	0.042743	0.2711	7.57E-08	0.00121	0.0104
2	5.08E-06	0.036096	0.30008	2.77E-07	0.00404	0.0389
2.2	4.66E-06	0.028777	0.27953	6.33E-08	0.000768	0.0102
2.4	4.21E-06	0.019849	0.26155	8.40E-08	0.000758	0.0155
2.6	3.67E-06	0.011736	0.21404	1.23E-07	0.000712	0.027
2.8	3.61E-06	0.0088516	0.18427	1.16E-07	0.000502	0.0261
3	3.20E-06	0.0058973	0.11845	8.73E-08	0.00026	0.0226
3.2	3.23E-06	0.0048614	0.14171	7.07E-08	0.000178	0.0179
3.5	3.11E-06	0.0032541	0.15057	8.99E-08	0.000159	0.0237
4	2.74E-06	0.0018165	0.085937	1.07E-07	0.000107	0.0327
4.5	2.63E-06	0.0010744	0.08542	7.66E-08	0.0000463	0.0247
5	2.24E-06	0.00078988	0.033971	2.57E-08	0.0000122	0.00982
5.5	2.15E-06	0.00047625	0	4.95E-08	0.0000202	–
6	2.01E-06	0.00038646	0	1.67E-08	0.00000608	–
6.5	1.78E-06	0.00027643	0	1.77E-08	0.00000546	–
7	1.78E-06	0.00020308	0	3.26E-08	0.00000742	–

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