Electronic Supplementary Material (ESI) for Dalton Transactions.

ESI

Slow Magnetic Relaxation in a Ferromagnetic Cu^{II} Chain Complex, Induced by Phonon Bottleneck Effect

Sailaja S. Sunkari,*[a] Abhineet Verma,[a] Om Pandey,[a] Shraddha Gupta,[b] Masanori Wakazaka,[b] Shinya Takaishi,[b] Hideyuki Kawasoko,[b] Tomoteru Fukumura,[b] and Masahiro Yamashita[b,c]

[a]Department of Chemistry, Mahila Mahavidyalaya, Banaras Hindu University, Varanasi 221 005, India,
[b]Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba, Aoba-Ku, Sendai 980-8578, Japan.
[c]School of Materials Science and Engineering, Nankai University, Tianjin 300350, China

Experimental Section

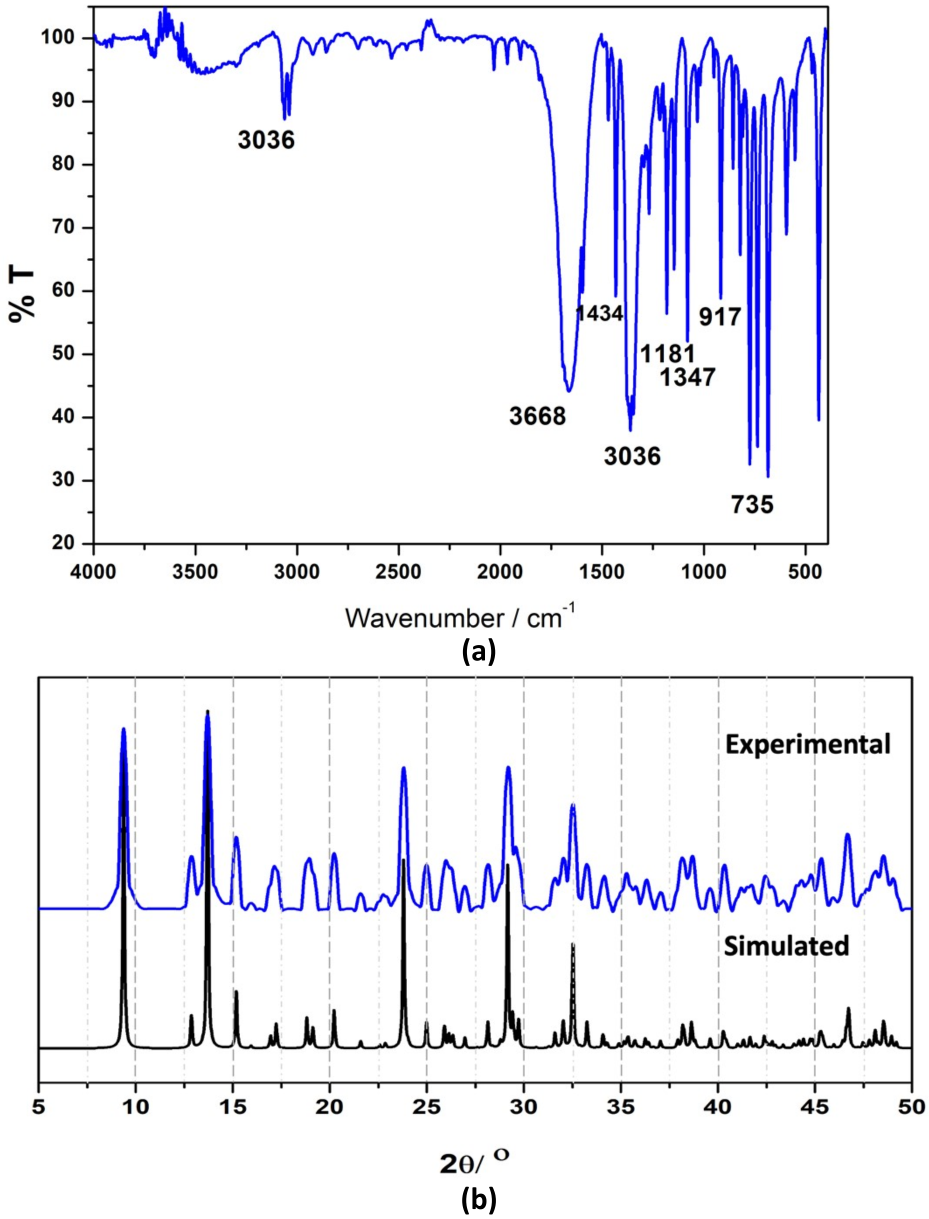
The starting material $Cu(CH_3COO)_2{\cdot}H_2O$ and dipicH$_2$ were procured from sigma Aldrich and were used directly without further purification. Infrared spectra were recorded using a PerkinElmer Spectrum-2 FTIR spectrometer over the range 400−4000 cm^{-1} using KBr pellets. Powder X-ray diffraction (PXRD) data were collected using a Bruker D8-ADVANCE diffractometer equipped with Cu-Kα1 radiation (λ = 1.5406 Å; 1600 W, 40 kV, 40 mA) at a scan speed of 5 K min^{-1}. Elemental analyses were measured using a Thermoscientific Flash 2000 Organic elemental analyser. For SCXRD data, a Rigaku Saturn 724 (based on a rotating anode as an X-ray generator, Mo−Kα radiation) was used to record diffraction data at 293 K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELX-2019. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Integrated intensity information for each reflection was obtained by reducing the data frames with the program APEX3. The absorption correction program SADABS was employed to correct the data for absorption effects. Drawings were made using OLEX-II and Mercury 3.0. Magnetic measurements were performed using a magnetic property measurement system (MPMS-XL, Quantum Design) in the direct current mode and the ac mode. The sample was filled into a gelatin capsule (Matsuya), which was fixed in a plastic straw. The heat capacity measurements were recorded in the liquid He cryostat of a Quantum Design PPMS (Physical Property Measuring System).

DFT calculation

DFT calculations of the triplet states of a dimer model, $[Cu^{II}(dipic)(H_2O)_2]_2$, were performed at an unrestricted UB3LYP/Lanl2DZ level of theory using the Gaussian 16W package.[S1,S2] The atomic coordinates used were those of the crystal structure without alteration (Table S4).

Synthesis

10 mL aqueous solution of $Cu(CH_3COO)_2{\cdot}H_2O$(0.199g, 1.0 mmol) was layered with 20 mL methanolic solution of $DipicH_2$ (0.334g, 2.0mmol) and was kept for diffusion at room temperature. After 3-5 days, blue rod-shaped crystals were obtained from the diffusion tube at RT, which was suitable for X-ray analysis. Yield: 0.151g (0.57 mmol, 57.02%); M.P = above 350 ^{o}C. Anal. calcd for $C_7H_7CuNO_6$ (M.W. = 264.7): C 31.77; H 2.67; N 5.29. Found C 31.26; H 2.13; N 5.37. FT-IR (**Figure S1** (**a**)) and PXRD (**Figure S1(b))** confirms bulk purity of the compound.



(a)

(b)

Figure S1. (a) FT-IR and (b) PXRD of the title complex [**DCu**].

Table S1. Important Crystal Data for **[DCu]**.

Empirical formula	$C_7H_7NO_6Cu$	**γ (°)**	90
CCDC No.	2231609	**V (Å^3)**	830.53(7)
F.W.	264.68	**T (K)**	110
Space group	$P2_1/c$	**Z**	4
Crystal system	Monoclinic	**D_{calc} (mg m^{-3})**	2.117
a (Å)	7.1916(3)	**μ (mm^{-1})**	2.639
b (Å)	18.8411(7)	**GOF on F^2**	1.0583
c (Å)	6.4145(3)	**R (F_o^2)^a**	0.0289
α (°)	90	**Rw (F_o^2)^b**	0.0681
β (°)	107.144(5)		

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

Table S2. Important bond length (Å), bond angles (°) and hydrogen bond (Å) interactions for [**DCu**].

Bond length / Å		
Cu1-O1 : 2.0433(11)	Cu1-O6 : 2.3672(12)	Cu1-O5 : 1.9459(11)
Cu1-O3 : 2.0636(11)	Cu1-O3^{I} : 2.4134(11)	Cu1-N1 : 1.9020(13)

^{I} = X, 3/2 - Y, Z+1/2

	Bond angle / °	
O1-Cu1-O6 : 90.16(4)	O1-Cu1-O3 : 160.62(5)	O1-Cu1-O3^{I} : 83.38(4)
O6-Cu1-O3^{I} : 169.59(4)	O5-Cu1-O1 : 95.31(5)	O5-Cu1-O6 : 88.64(5)
O5-Cu1-O3 : 104.06(5)	O5-Cu1-O3^{I} : 83.86(4)	O3-Cu1-O6 : 89.60(4)
O3-Cu1-O3^{I} : 99.19(4)	N1-Cu1-O1 : 80.32(5)	N1-Cu1-O6 : 95.37(5)
N1-Cu1-O5 : 174.05(5)	N1-Cu1-O3 : 80.41(5)	N1-Cu1- O3^{I} : 91.59(5)

^{I} = X, 3/2 - Y, Z+1/2

Hydrogen bond/ Å

D-H···A	**d(D-H)/ Å**	**d(H-A)/ Å**	**d(D-A)/ Å**	**D-H---A / °**
O5-H5b···O1^{I}	0.85	1.810(2)	2.6238(16)	159.7(4)
O6-H6A···O2^{II}	0.85	1.915(3)	2.7465(17)	165.5(12)

^{I} = X, 3/2 – Y, Z-1/2; ^{II} = X, Y, Z-1

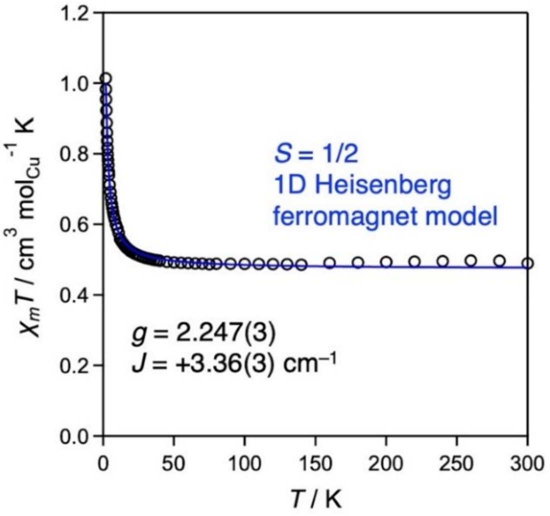


Figure S2. $\chi_m T$–T plots together with the fitting curve (blue line) and fitting parameters of [**DCu**].

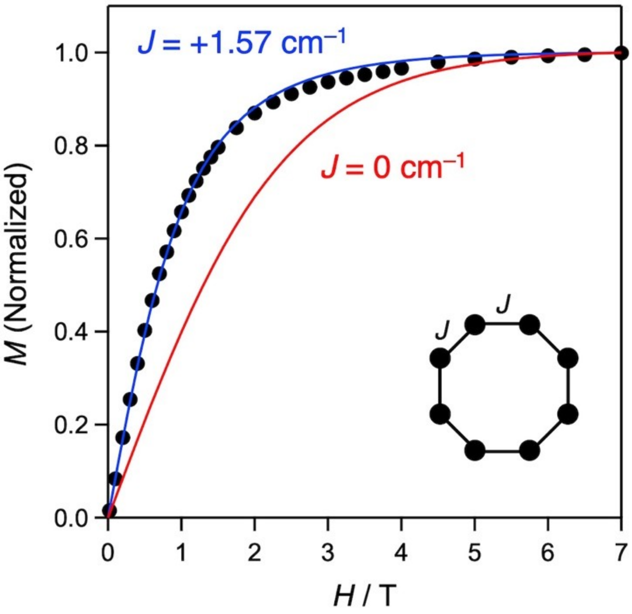


Figure S3. The normalized magnetization–field curve at 1.8 K, together with those of simulations (blue and red curves) of J = +1.57 and 0 cm^{-1} with g_{iso} = 2.252, using the program PHI.[14]

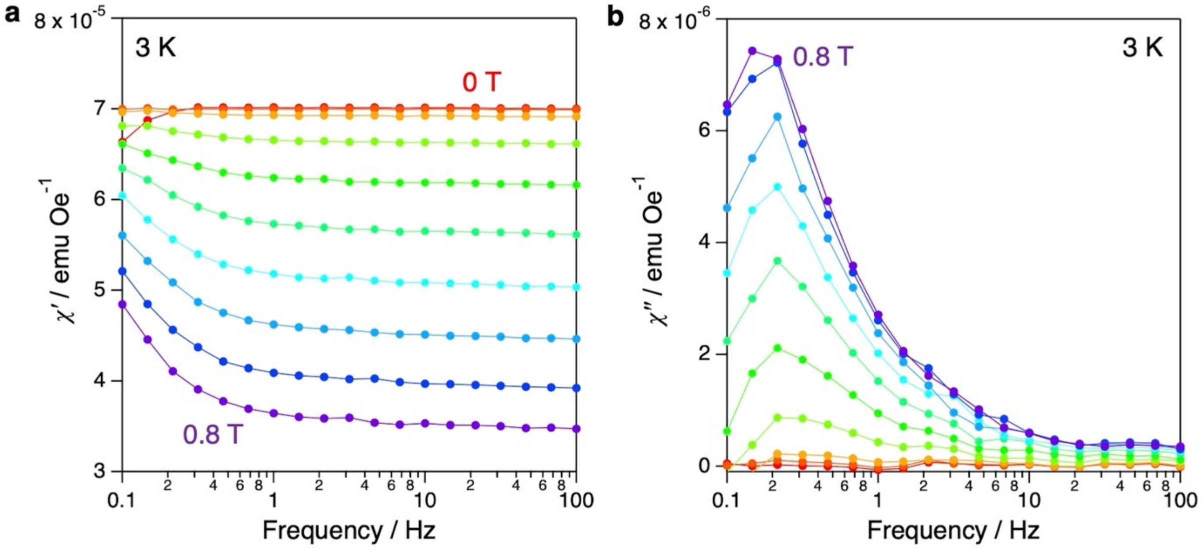


Figure S4. (a) The in-phase component (χ') and (b) the out-of-phase component (χ'') of AC susceptibility of [**DCu**] measured at 3 K under magnetic field of 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 T. AC drive is 2.5 Oe.

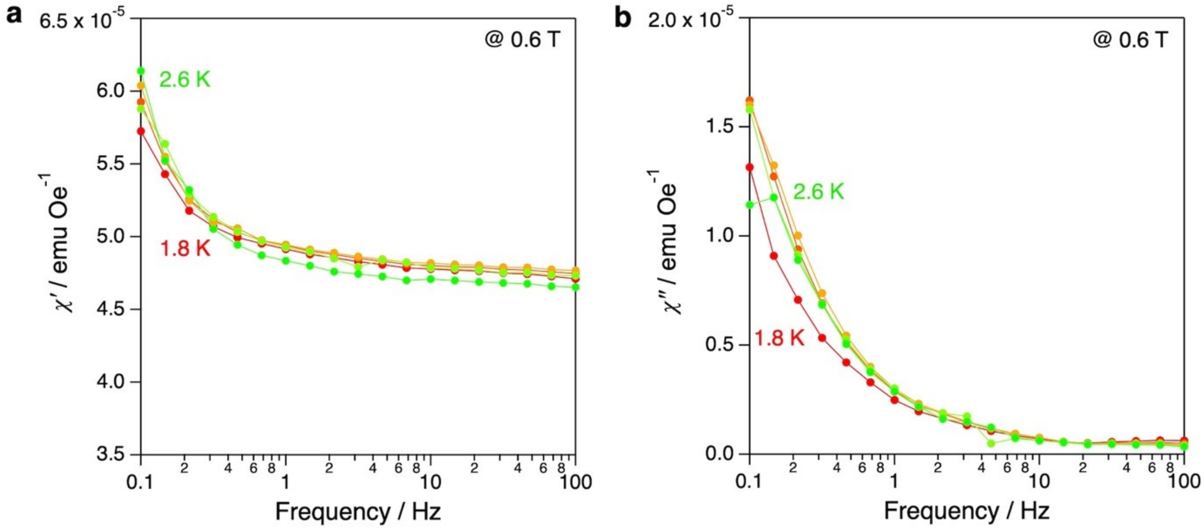


Figure S5. (a) The in-phase component (*χ′*) and (b) the out-of-phase component (*χ″*) of AC susceptibility of [**DCu**] measured at 1.8–2.6 K under magnetic field of 0.6 T. AC drive is 2.5 Oe.

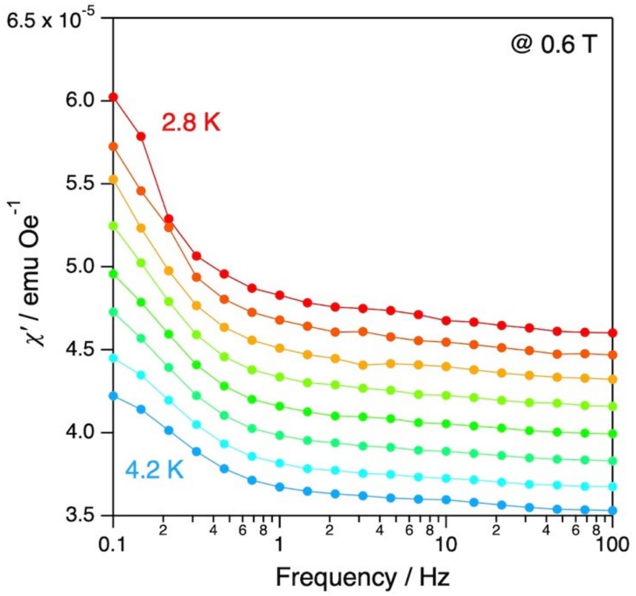


Figure S6. The in-phase component of AC susceptibility (*χ′*) of [**DCu**], measured at 2.8–4.2 K, under a static magnetic field of 0.6 T. AC drive is 2.5 Oe.

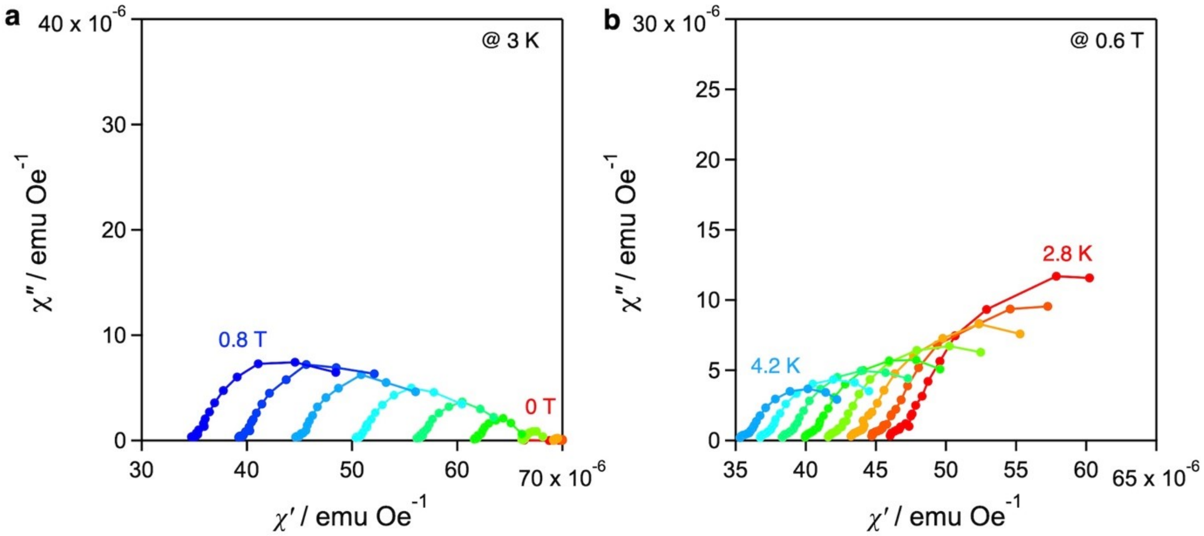


Figure S7. Cole-Cole plots of AC susceptibility of [**DCu**], measured at (a) 3 K under 0, 0.05, 0.1, 0.2 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 T; and (b) at 2.8, 3.0, 3.2, 3.5, 4.0, and 4.2 K under 0.6 T.

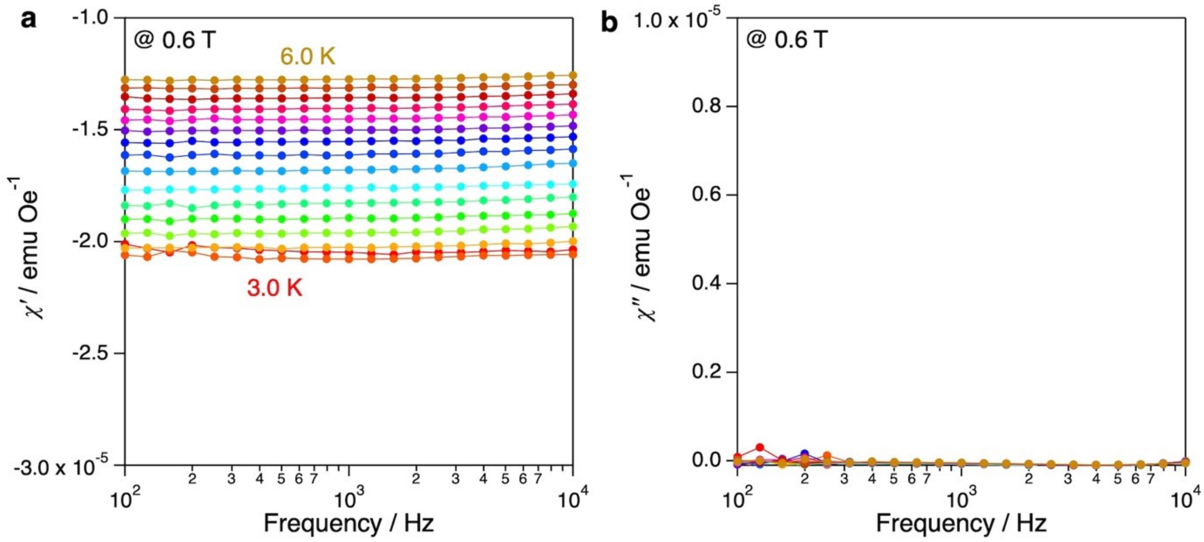


Figure S8. The in-phase component (χ') and (b) the out-of-phase component (χ'') of AC susceptibility of [**DCu**] measured at 3.0–6.0 K under magnetic field of 0.6 T. AC drive is 5 Oe.

Table S3. AC susceptibility fitting data of the imaginary part of [**DCu**]

T [K]	$\chi_T - \chi_S$ [emu/Oe]	τ [s]	β	$\sigma(\chi_T - \chi_S)$ [emu/Oe]	$\sigma\tau$ [s]	$\sigma\beta$
2.8	2.74E-05	2.20	0.75	1.4E-06	0.30	0.04
3.0	2.29E-5	2.08	0.70	8.8E-07	0.24	0.03
3.2	1.86E-05	1.66	0.73	5.7E-07	0.16	0.03
3.4	1.56E-05	1.47	0.72	4.1E-07	0.13	0.03
3.6	1.33E-05	1.30	0.72	3.3E-07	0.11	0.03
3.8	1.16E-05	1.24	0.71	2.6E-07	0.09	0.03
4.0	9.96E-06	1.10	0.71	2.4E-07	0.09	0.03
4.2	8.65E-06	1.08	0.68	2.0E-07	0.08	0.03

Standard deviation (σ).

Table S4. Cartesian coordinates of $[Cu^{II}(dipic)(H_2O)_2]_2$

Number	Atomic number	*x* (Å)	*y* (Å)	*z* (Å)
1	29	1.905506	-0.915765	0.101918
2	8	3.818418	-1.45249	0.578837
3	8	5.831061	-0.54763	0.978181
4	8	0.296071	0.231372	-0.491745
5	8	-0.2637	2.383422	-0.813562
6	8	1.146005	-2.684574	0.386009
7	1	1.193394	-3.130488	-0.337485
8	1	0.312327	-2.614243	0.536437
9	8	2.295138	-1.507799	-2.156717
10	1	1.965826	-0.912668	-2.666997
11	1	1.86007	-2.213368	-2.344014
12	7	2.752244	0.7837	-0.010503
13	6	4.046832	0.871378	0.289094
14	6	4.704822	2.092179	0.245969
15	1	5.624444	2.164488	0.474315
16	6	3.966158	3.207931	-0.14461
17	1	4.390176	4.05653	-0.19643
18	6	2.608811	3.0932	-0.461091
19	1	2.105285	3.850416	-0.738088
20	6	2.018228	1.842438	-0.359486
21	6	4.645726	-0.466512	0.65319
22	6	0.555978	1.487096	-0.576557
23	29	-1.853522	-0.834803	-0.75107
24	8	-1.284551	-1.856074	0.924707
25	8	-1.33096	-1.693439	3.160934
26	8	-2.770842	0.56171	-1.962112
27	8	-3.853028	2.52554	-1.817795
28	8	-0.898772	-1.985794	-1.996141
29	1	-1.404031	-2.630917	-2.226653
30	1	-0.753488	-1.562598	-2.71885
31	8	-3.739529	-2.247225	-0.979739
32	1	-4.422315	-1.779523	-1.174573
33	1	-3.631973	-2.757212	-1.650943
34	7	-2.626541	0.280785	0.581526
35	6	-2.431748	-0.028076	1.862193
36	6	-2.954208	0.767232	2.871939
37	1	-2.805184	0.561859	3.787807
38	6	-3.705299	1.878594	2.492567
39	1	-4.087341	2.436548	3.15966
40	6	-3.903198	2.18171	1.141694
41	1	-4.423875	2.932744	0.879996
42	6	-3.318008	1.35477	0.194466
43	6	-1.61673	-1.288048	2.033365
44	6	-3.329574	1.522332	-1.316535

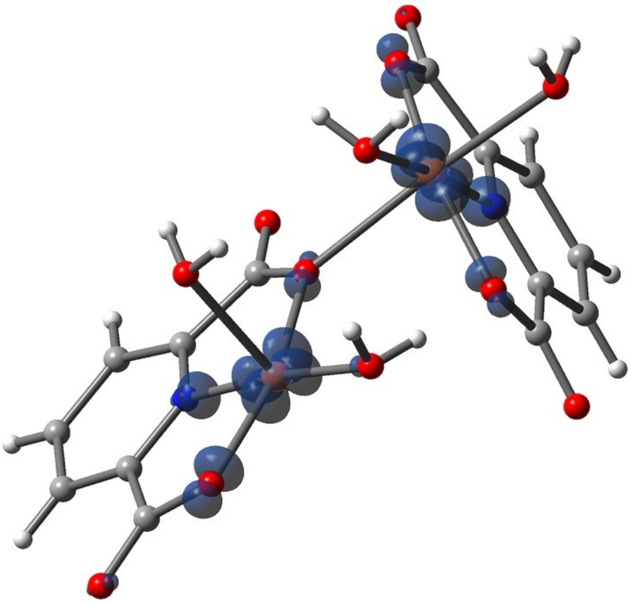


Figure S9. The spin density surface of the triplet state of a dimer model of [**DCu**] with an isovalue of 0.02 calculated at the UB3LYP/Lanl2DZ level of theory using the Gaussian 16W package.[S1,S2]

References

[S1] Gaussian 16W, Revision 1.1, Gaussian, Inc., Wallingford CT, 2016.

[S2] GaussView, Version 6.1.1, Semichem Inc., Shawnee Mission, KS, 2016.