Supplementary Information

A One-Dimentional Coordination Polymer Constructed from Planar Pentanuclear Copper(II) Clusters with a Flexible Tripodal Ligand

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Materials and Methods:

All reagents and solvents used were received from commercial suppliers without further purification. Elemental analyses (C, H, and N) were performed with a Vario MICRO CHNOS elemental analyzer. The infrared spectra with KBr pellet were recorded in the range of 4000–400 cm^{-1} on a Perkin-Elmer Spectrum One FT-IR spectrometer. Thermal analyses were performed on a NETZSCH STA 449C instrument from room temperature to 800 °C with a heating rate of 10 °C min^{-1} under nitrogen flow. Powder X-ray diffraction (PXRD) data were collected on a DMAX-2500 diffractometer with Cu K_α. The calculated patterns were generated with PowderCell. Magnetic susceptibility was measured on polycrystalline samples by using a Quantum Design MPMS-XL SQUID magnetometer.

Synthesis of Complex 1:

Tris(2-carboxyethyl)isocyanurate (0.138 g, 0.40 mmol) was added to an aqueous solution (10 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1.00 mmol) to give a blue solution. A blue precipitate was formed when the NaOH (0.5 M) solution was added slowly. Vigorous stirring readily dissolved it. The addition of NaOH solution and stirring were continued until irreversible precipitation occurred. The solution was filtered and exposed to air for slow evaporation. Blue-turquoise crystals were obtained about a week later. The crystals were isolated by filtration, washed with water, and dried in the air. Yield: 0.226 g (78 % based on H_3tic). Elemental analysis (%) calcd for $Cu_5C_{24}H_{50}N_6O_{40}Cl_2$: C 19.86, H 3.47, N 5.79; found: C 19.73, H 3.43, N 5.81. The IR spectrum of **1** is shown in **Fig S5**.

Crystallographic Analyses:

The structural determination of single crystal was performed on Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at room temperature. The collected data were reduced using the program CrystalClear (Rigaku and MSC, 1999) and an empirical absorption correction (SADABS) was applied. The structure was solved by direct methods and refined by the full-matrix

least-squares technique on F^2 using the SHELXTL-97 program.[1] All non-hydrogen atoms except some of the oxygen atoms from free water molecules and ClO_4^- were refined with anisotropic displacement parameters. The positions of hydrogen atoms attached to carbon and nitrogen atoms were generated geometrically (C-H bond fixed at 0.97 Å); and those on μ_3-OH groups were located in a difference Fourier map and refined with O-H distance restraints of 0.85(1), while those on free water molecules could not be reliably located but are included in the formula. During the refinement, there were a number of short connections between O(water)···O(coordination chain) in the range of 2.50–2.90 Å, suggesting extensive H-bonding interactions between lattice water molecules and the coordination chains. One of the ClO_4^- anions was found to be disordered over two positions around the Cl atom; the displacement parameters for the two parts of each O atom were constrained to be equal. Additionally, the water molecules O5W and O9W have refined to occupancies of 65% and 35%, respectively. Crystallographic data and structure determination summaries are listed in Table S1. Selected bond lengths and angles of complex **1** are listed in Table S2.

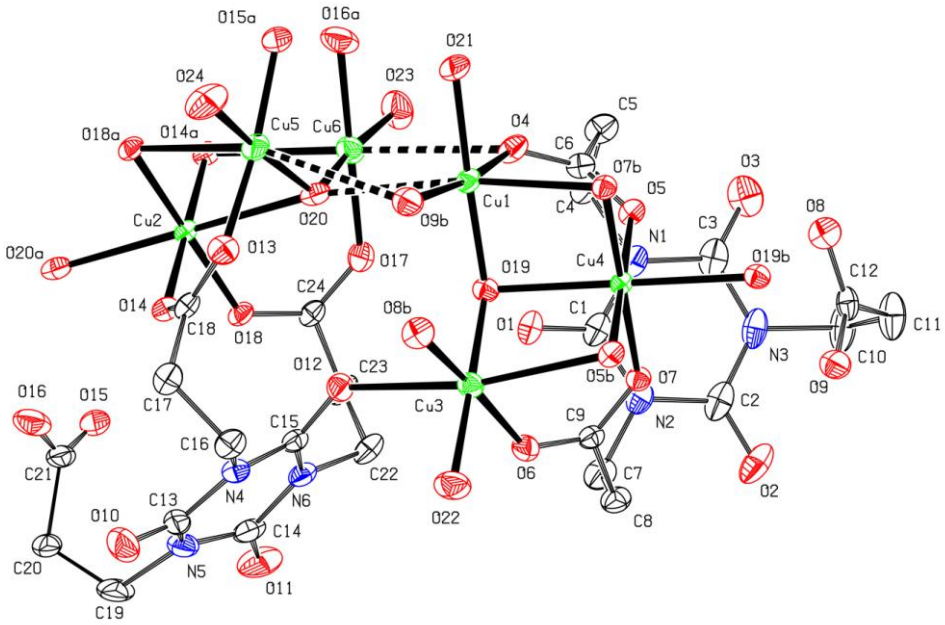


Fig. S1 ORTEP diagram showing the coordination environments for Cu(II) atoms with a 30% probability level in **1**. Lattice water molecules, perchlorate anions and hydrogen atoms are omitted for clarity. Symmetry codes for the generate atoms: a, 1–x, 1–y, –z; b, 1–x, 1–y, –1–z.

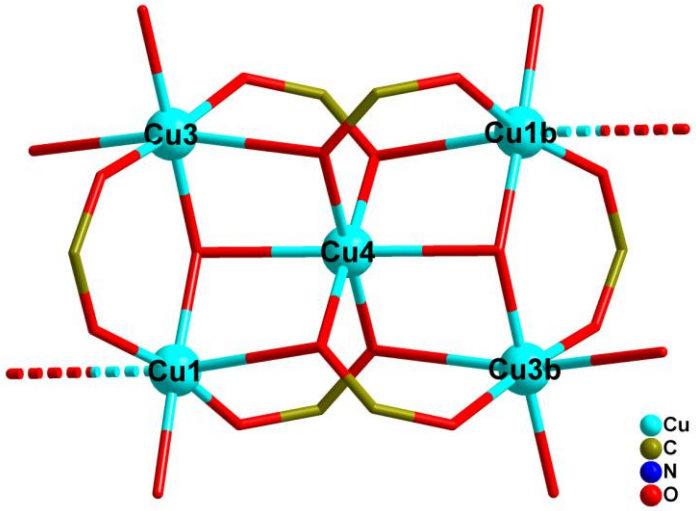
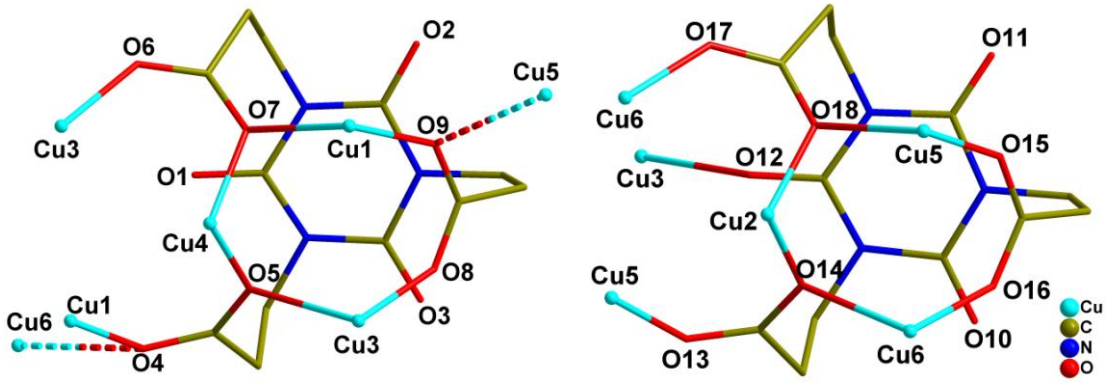


Fig. S2 The pentanuclear copper(II) core in type II pentanuclear copper(II) cluster. Symmetry code: b, 1–x, 1–y, –1–z. Selected distances and angles are Cu1···Cu4 3.0816(5), Cu3···Cu4 3.1149(5), Cu1···Cu3 3.4640(8) and Cu1···Cu3b 5.1379(7) Å; Cu1–Cu3–Cu1b 89.34 and Cu3–Cu1–Cu3b 90.66°.



(a) **(b)**

Fig. S3 Coordination modes of the ligand (a) in type I pentanuclear copper(II) cluster and (b) in type II pentanuclear copper(II) cluster.

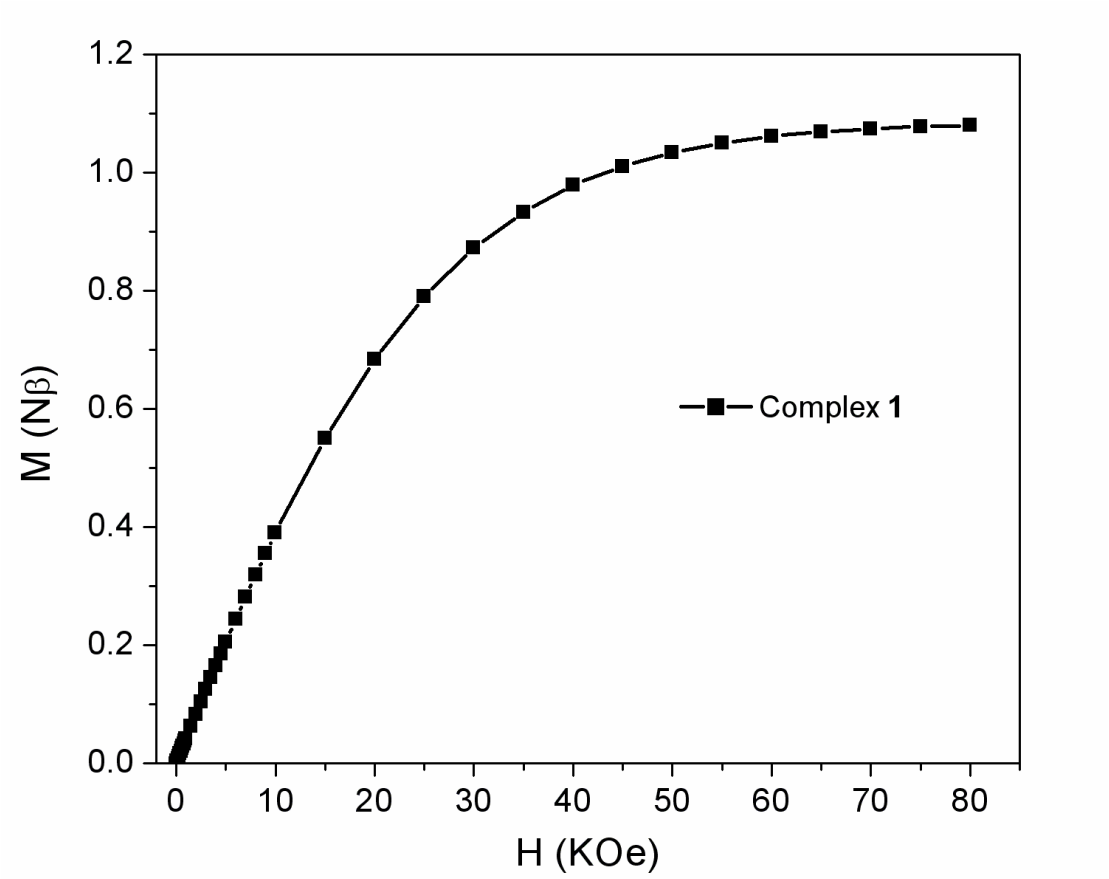


Fig. S4 The isothermal field-dependent magnetization plots for **1** at 2 K**.**

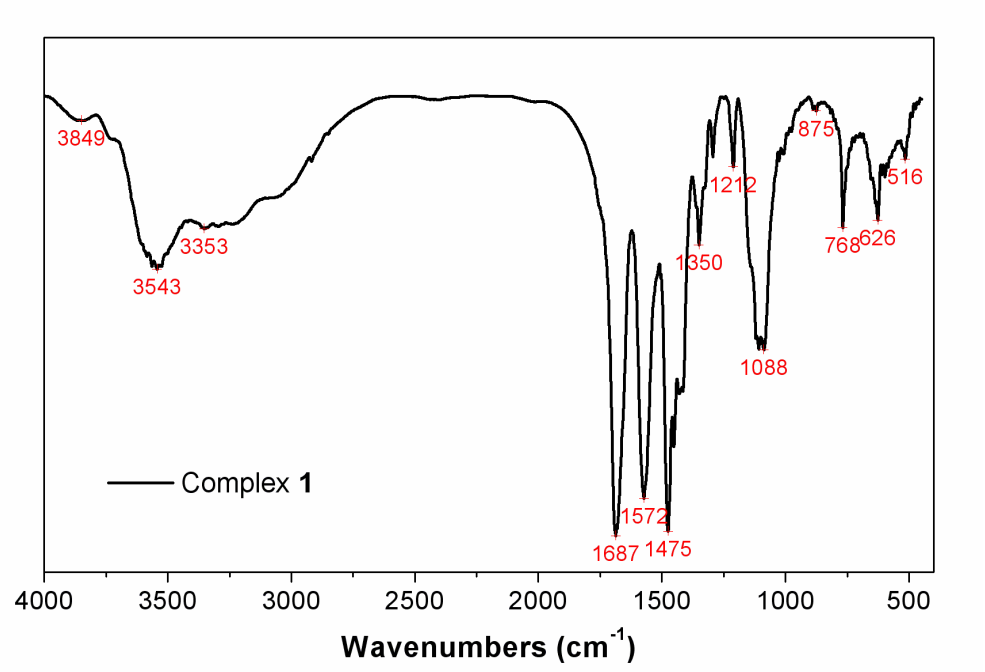


Fig. S5 IR spectra of **1**.

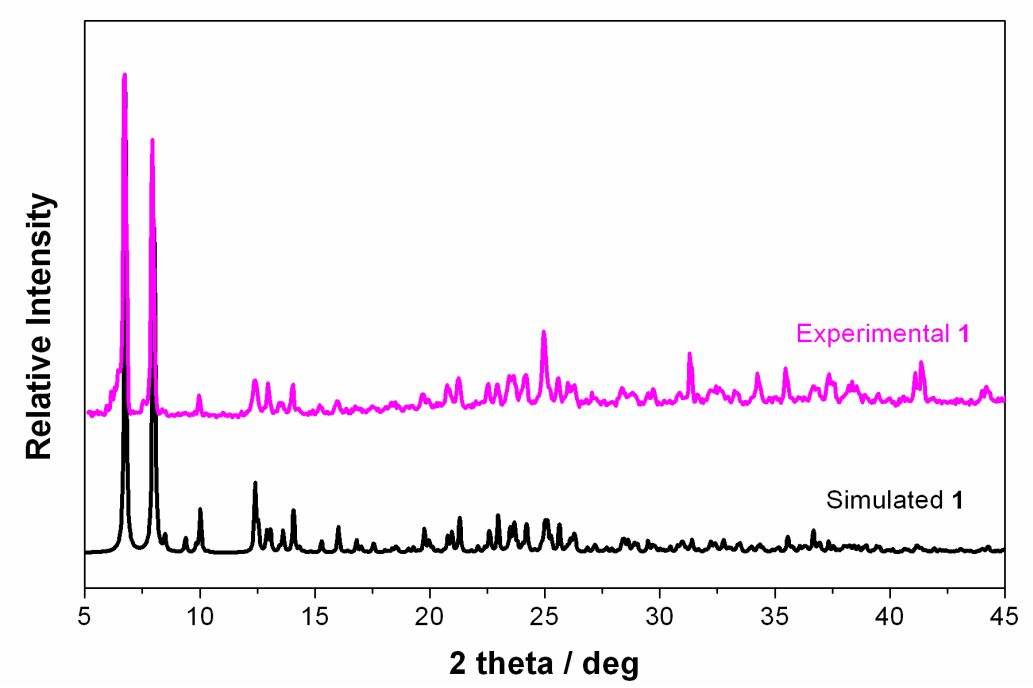


Fig. S6 Powder X-ray diffractions for simulated and experimental **1**.

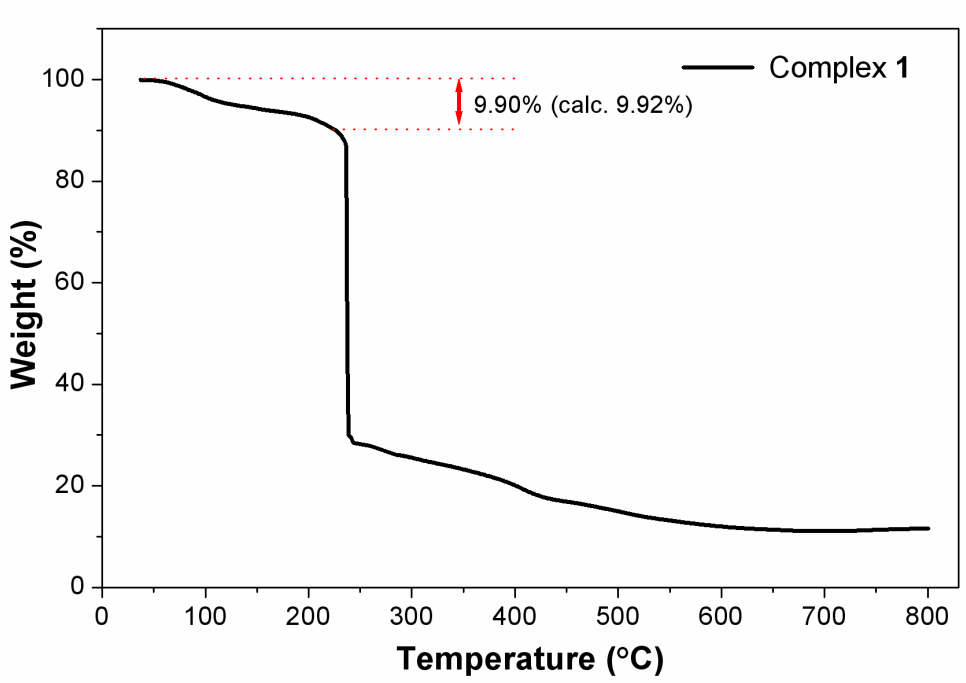


Fig. S7 TGA curve of complex **1.**

Table S1. Crystal Data and Structure Refinements for **1**

Compound	**1**
Formula	$Cu_5C_{24}H_{50}N_6O_{40}Cl_2$
*M*r [g mol^{-1}]	1451.30
Temperature	293 K
Cryst syst	triclinic
Space group	*P-1*
a (Å)	12.2174(12)
b (Å)	14.3962(13)
c (Å)	15.2425(9)
α (deg)	93.545(3)
β (deg)	93.921(2)
γ (deg)	114.081(4)
V (Å^3)	2430.0(4)
Z	2
D_c (g cm^{-3})	1.984
μ (mm^{-1})	2.385
Reflns collcd	21157
Unique reflns (R_{int})	11011 (0.0306)
S on F^2	0.992
R1,[a] wR2[b] [$I>2\sigma(I)$]	0.0480, 0.1363
R1,[a] wR2[b] (all data)	0.0594, 0.1462

[a] $R1 = \sum(||Fo| - |Fc||)/\sum|Fo|$, [b] $wR2 = \{\sum w[(F_o^2 - F_c^2)^2]/\square\sum w[(F_o^2)^2]\}^{1/2}$.

Table S2. Selected Bond Lengths [Å] and Angles [°] for Complex **1**[a]

Cu1-O19	1.906(3)	Cu3-O8b	1.942(3)	Cu5-O13	1.932(3)
Cu1-O9b	1.928(3)	Cu3-O22	1.949(3)	Cu5-O24	1.952(3)
Cu1-O21	1.941(3)	Cu3-O6	1.962(3)	Cu5-O18a	2.554(2)
Cu1-O4	1.945(3)	Cu3-O12	2.528(3)	Cu5-O9b	3.006(3)
Cu1-O20	2.801(3)	Cu3-O15b	2.577(3)	Cu6-O20	1.909(3)
Cu1-O7b	2.490(3)	Cu4-O7	1.984(2)	Cu6-O16a	1.931(4)
Cu2-O18	1.949(2)	Cu4-O5	1.990(2)	Cu6-O23	1.937(3)
Cu2-O14	1.963(2)	Cu4-O19	2.293(3)	Cu6-O17	1.949(3)

Cu2-O20	2.503(3)	Cu5-O20	1.900(3)	Cu6-O4	2.916(3)
Cu3-O19	1.893(3)	Cu5-O15a	1.903(4)	Cu6-O14a	2.558(3)
O19-Cu1-O9b	95.66(12)	O7b-Cu4-O5	89.06(11)	O13-Cu5-O24	86.43(15)
O19-Cu1-O21	176.85(11)	O7-Cu4-O5	90.94(11)	O20-Cu6-O16a	94.68(15)
O9b-Cu1-O21	87.45(13)	O7b-Cu4-O5b	90.94(11)	O20-Cu6-O23	173.47(13)
O19-Cu1-O4	89.69(11)	O7-Cu4-O5b	89.06(11)	O16a-Cu6-O23	87.73(17)
O9b-Cu1-O4	169.76(13)	O5-Cu4-O5b	180	O20-Cu6-O17	90.47(12)
O21-Cu1-O4	87.30(12)	O7b-Cu4-O19b	91.12(10)	O16a-Cu6-O17	174.69(15)
O18-Cu2-O18a	180	O7-Cu4-O19b	88.88(10)	O23-Cu6-O17	87.30(15)
O18-Cu2-O14a	90.61(11)	O5-Cu4-O19b	90.02(10)	Cu3-O19-Cu1	131.49(14)
O18a-Cu2-O14a	89.39(11)	O5b-Cu4-O19b	89.98(10)	Cu3-O19-Cu4	95.67(11)
O18-Cu2-O14	89.39(11)	O7b-Cu4-O19	88.88(10)	Cu1-O19-Cu4	93.95(11)
O18a-Cu2-O14	90.61(11)	O7-Cu4-O19	91.12(10)	Cu3-O5b-Cu4	84.98(9)
O14a-Cu2-O14	180	O5-Cu4-O19	89.98(10)	Cu1-O7b-Cu4	86.27 (9)
O19-Cu3-O8b	95.10(12)	O5b-Cu4-O19	90.02(10)	Cu5-O20-Cu6	130.06(15)
O19-Cu3-O22	176.92(14)	O19b-Cu4-O19	180	Cu2-O20-Cu5	88.33(10)
O8b-Cu3-O22	86.93(14)	O20-Cu5-O15a	95.49(14)	Cu2-O20-Cu6	88.71(10)
O19-Cu3-O6	91.05(11)	O20-Cu5-O13	92.54(12)	Cu2-O18a-Cu5	85.82(9)
O8b-Cu3-O6	173.56(13)	O15a-Cu5-O13	171.92(14)	Cu2-O14a-Cu6	85.99(9)
O22-Cu3-O6	87.01(13)	O20-Cu5-O24	171.91(16)		
O7-Cu4-O7b	180	O15a-Cu5-O24	85.73(17)		

[a] Symmetry codes: (a) -x+1,-y+1,-z; (b) -x+1,-y+1,-z-1.

[1] *SHELXTL*, version 5.10; Siemens Analytical X-ray Instruments Inc.: Madison, WI, **1994**.