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Supporting Information

A New Class of Hydroxo-Bridged Heptacopper(II) Clusters with an Acentrosymmetric Corner-Sharing Double-Cubane Framework Supported by D-Penicillaminedisulfides

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[A] Experimental Procedures.

Preparation of $[Cu_7(\mu_3\text{-}OH)_6(\mu_3\text{-}Cl)_2(\textsc{d}\text{-pends})_3]$ (1). To a stirred dark brown solution containing 0.10 g (0.23 mmol) of K[Co(D-pen-*N,O,S*)$_2$]·2.5H_2O in 5 mL of water was added 0.06 g (0.48 mmol) of $CuCl_2$ in 5 mL of water. The mixture was stirred at RT for 1 h, and then filtered. The filtrate was allowed to stand at RT for 3 days, and the resulting blue trigonal-pyramidal crystals were collected by filtration. Yield: 0.034 g (19 %); elemental analysis calcd (%) for $[Cu_7(\mu_3\text{-}OH)_6(\mu_3\text{-}Cl)_2(\text{D-pends})_3]\cdot 20H_2O$: C 19.36, H 5.42, N 4.52; found: C 19.33, H 5.20, N 4.51. Reflection spectrum in the solid state [λ_{max}, nm]: 697. CD spectrum in the solid state [$\lambda_{extrema}$, nm]: 557 (–). IR spectrum (KBr disk, cm^{-1}): 1636 (ν_{COO^-}).

Preparation of $[Cu_7(\mu_3\text{-}OH)_6(\mu_3\text{-}Cl)_2(\textsc{l}\text{-pends})_3]$ (1'). To a stirred dark brown solution containing 0.05 g (0.17 mmol) of K[Co(L-pen-*N,O,S*)$_2$]·2.5H_2O in 2.5 mL of water was added 0.03 g (0.24 mmol) of $CuCl_2$ in 2.5 mL of water. The mixture was stirred at RT for 1 h, and then filtered. The filtrate was allowed to stand at RT for 8 days, and the resulting blue trigonal-pyramidal crystals were collected by filtration. Elemental analysis calcd (%) for $[Cu_7(\mu_3\text{-}OH)_6(\mu_3\text{-}Cl)_2(\text{L-pends})_3]\cdot 20H_2O$: C 19.36, H 5.42, N 4.52; found: C 19.30, H 5.31, N 4.49. Reflection spectrum in the solid state [λ_{max}, nm]: 680. CD spectrum in the solid state [$\lambda_{extrema}$, nm]: 556 (+). IR spectrum (KBr disk, cm^{-1}): 1634 (ν_{COO^-}).

Preparation of $[Cu_7(\mu_3\text{-}OH)_6(\mu_3\text{-}Br)_2(\textsc{d}\text{-pends})_3]$ (2). To a stirred dark brown solution containing 0.10 g (0.23 mmol) of K[Co(D-pen-*N,O,S*)$_2$]·2.5H_2O in 5 mL of water was added 0.10 g (0.47 mmol) of $CuBr_2$ in 5 mL of water. The mixture was allowed to stand at RT for 1 h, and then filtered. The filtrate was allowed to stand at room temperature for 3 days, and the resulting blue trigonal-pyramidal crystals were collected by filtration. Yield: 0.025 g (15 %); elemental analysis calcd (%) for $[Cu_7(\mu_3\text{-}OH)_6(\mu_3\text{-}Br)_2(\text{D-pends})_3]\cdot 20.5H_2O$: C 18.39, H 5.20, N 4.29; found: C 18.42, H 5.12, N 4.29. Reflection spectrum in the solid state [λ_{max}, nm]: 688. CD spectrum in the solid state [$\lambda_{extrema}$, nm]: 578 (–). IR spectrum (KBr disk, cm^{-1}): 1636 ($\nu_{\mathrm{COO^-}}$).

Preparation of [$\mathbf{Cu_2}$(D-pends)$_\mathbf{2}$($\mathbf{H_2O}$)$_\mathbf{2}$] (3). To a dark brown solution containing 0.20 g (0.47 mmol) of K[Co(D-pen-*N,O,S*)$_2$]$\cdot$2.5H_2O in 10 mL of water was added 0.24 g (0.96 mmol) of $CuSO_4\cdot 5H_2O$ in 10 mL of water. The mixture was stirred at RT for 1 h, followed by allowing to stand at RT for 1 day. After filtration, the filtrate was further allowed to stand at RT for one week, and the resulting blue block crystals were collected by filtration. Yield: 0.036 g (18 %); elemental analysis calcd (%) for [Cu_2(D-pends)$_2$(H_2O)$_2$]$\cdot$6.5H_2O: C 27.64, H 6.15, N 6.45; found: C 27.49, H 5.98, N 6.42. Reflection spectrum in the solid state [λ_{max}, nm]: 631. CD spectrum in the solid state [$\lambda_{\mathrm{extrema}}$, nm]: 614 (+). IR spectrum (KBr disk, cm^{-1}): 1615 ($\nu_{\mathrm{COO^-}}$). This complex was obtained in a higher yield (47%) when K[Co(D-pen-*N,O,S*)$_2$]$\cdot$2.5H_2O was reacted with $CuSO_4\cdot 5H_2O$ in a 1:1 molar ratio. The use of $Cu(BF_4)_2$, $Cu(NO_3)_2$, and $Cu(ClO_4)_2$, instead of $CuSO_4$, also gave **3** in yields of 29%, 27%, and 24%, respectively.

X-ray Structural Determinations. Single-crystal X-ray diffraction experiments for **1** and **2** were performed on a Bruker AXS SMART-1000/CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 210 K for **1** and 200 K for **2**, respectively. The intensity data were collected by the ω–2θ scan technique and were empirically corrected for absorption with using the program SADABS. Single-crystal X-ray diffraction experiments for **3** were performed on a Rigaku RAXIS-RAPID imaging plate area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 200 K. The intensity data were collected by the ω scan technique and were empirically corrected for absorption. The structure was solved by the direct method with SIR97 or SIR92 and refined with full-matrix least-squares on F^2 using SHELXL-97. Crystal structure analysis for **1**$\cdot$21H_2O: $C_{30}H_{102}Cl_2Cu_7N_4O_{39}S_6$, crystal size 0.22 x 0.20 x 0.10 mm, trigonal, space group $P3_2$, a = 15.0898(9) Å, c = 27.315(2) Å, V = 5386.4(6) Å^3, Z = 3, ρ_{calcd} = 1.738 g cm^{-1}, μ = 2.373 mm^{-1}, ω–2θ scan mode, 2θ_{max} = 55.0, 39402 reflections collected, 13374 independent reflections, 11774 observed reflections ($I > 2\sigma(I)$), 840 parameters, semiempirical absorption corrections with SADABS, max./min.

transmission 0.6942/0.6062, $R1$ ($I > 2\sigma(I)$) = 0.0366, $wR2$ (all data) = 0.0684, Flack parameter 0.005(10), residual electron density 0.76/–0.57 e Å^{-3}. The inner Cu^{II} ion is disordered in two positions with site occupancy factors of 0.9 (Cu1) and 0.1 (Cu1B), which are situated in a coordination environment very similar to each other. Hydrogen atoms were not included in the calculations. Crystal structure analysis for **2**·21H$_2$O: $C_{30}H_{102}Br_2Cu_7N_4O_{39}S_6$, crystal size 0.15 x 0.10 x 0.10 mm, trigonal, space group $P3_2$, a = 15.1101(8) Å, c = 27.6093(19) Å, V = 5459.1(6) Å^3, Z = 3, ρ_{calcd} = 1.796 g cm^{-1}, μ = 3.366 mm^{-1}, ω–2θ scan mode, $2\theta_{max}$ = 55.0, 40376 reflections collected, 16692 independent reflections, 12429 observed reflections ($I > 2\sigma(I)$), 836 parameters, semiempirical absorption corrections with SADABS, max./min. transmission 0.8014/0.6389, $R1$ ($I > 2\sigma(I)$) = 0.0433, $wR2$ (all data) = 0.0776, Flack parameter 0.005(7), residual electron density 0.96/–0.53 e Å^{-3}. The inner Cu^{II} ion is disordered in two positions with site occupancy factors of 0.9 (Cu1) and 0.1 (Cu1B). Hydrogen atoms were not included in the calculations. CCDC-648594 (**1**·21H$_2$O) and CCDC-648595 (**2**·21H$_2$O) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal structure analysis for **3**·7.5H$_2$O: $C_{20}H_{55}Cu_2N_4O_{17.5}S_4$, Space group $C2$, a = 12.230(5) Å, b = 19.687(6), c = 15.488(4) Å, b = 91.988(13)°, V = 3727(2) Å^3, Z = 4, r_{calcd} = 1.581 g cm^{-1}, μ = 1.438 mm^{-1}, ω scan mode, $2\theta_{max}$ = 55°, 18207 reflections collected, 7949 independent reflections, 7060 observed reflections ($I > 2\sigma(I)$), 430 parameters, empirical absorption corrections, max./min. transmission 0.9316/0.7150, $R1$ ($I > 2\sigma(I)$) = 0.0404, $wR2$ (all data) = 0.1075, Flack parameter 0.009(11), residual electron density 0.53/–0.45 e Å^{-3}.

[B] Absorption and CD Spectra of Complexes.

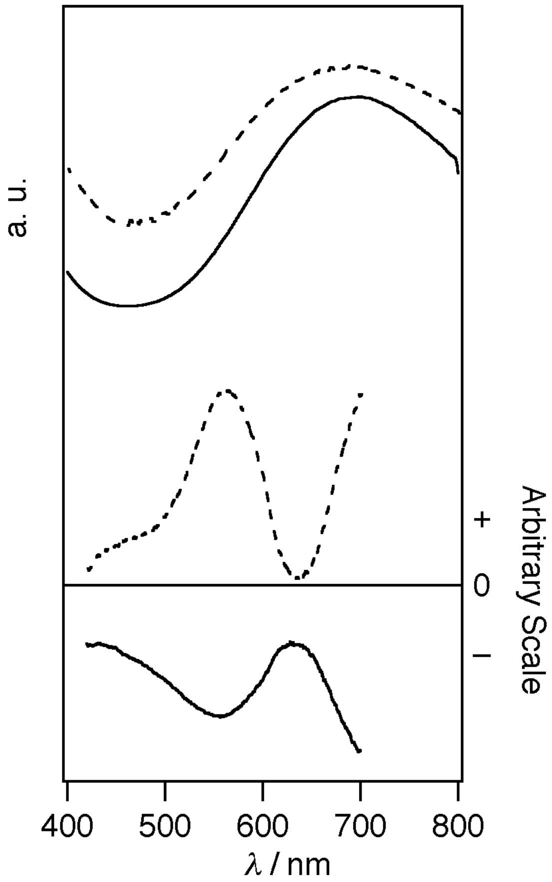

Figure S1. Absorption (top) and CD (bottom) spectra of **1** (—) and **1’** (---) in the solid state.

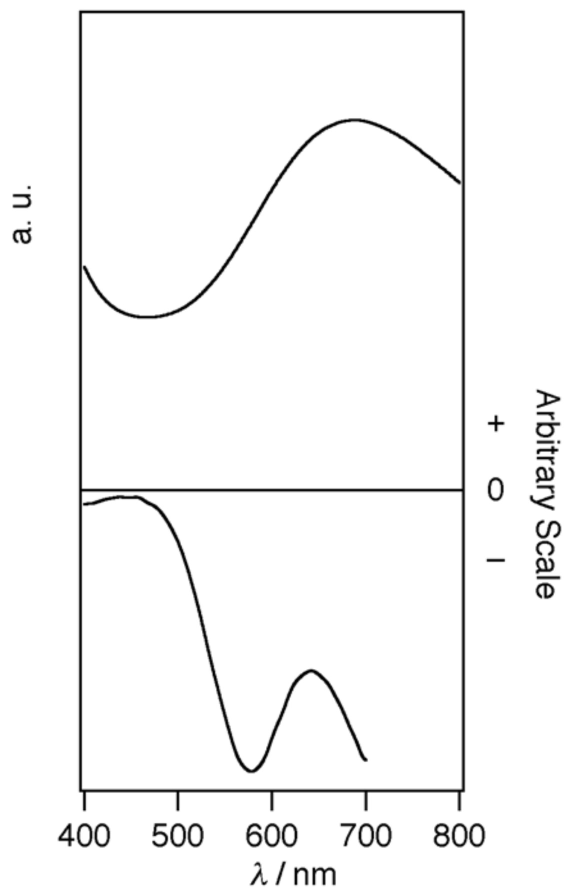

Figure S2. Absorption (top) and CD (bottom) spectra of **2** in the solid state.

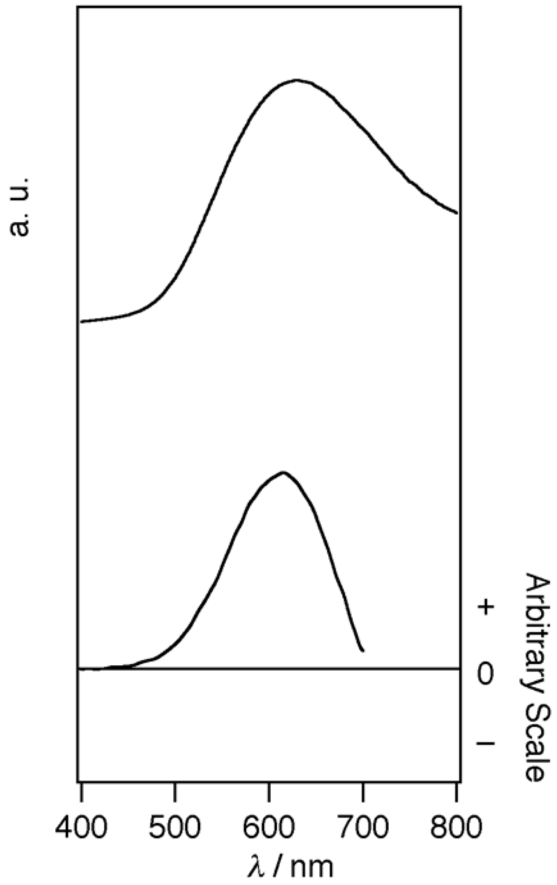

Figure S3. Absorption (top) and CD (bottom) spectra of **3** in the solid state.

[C] Crystal Structures of Complexes

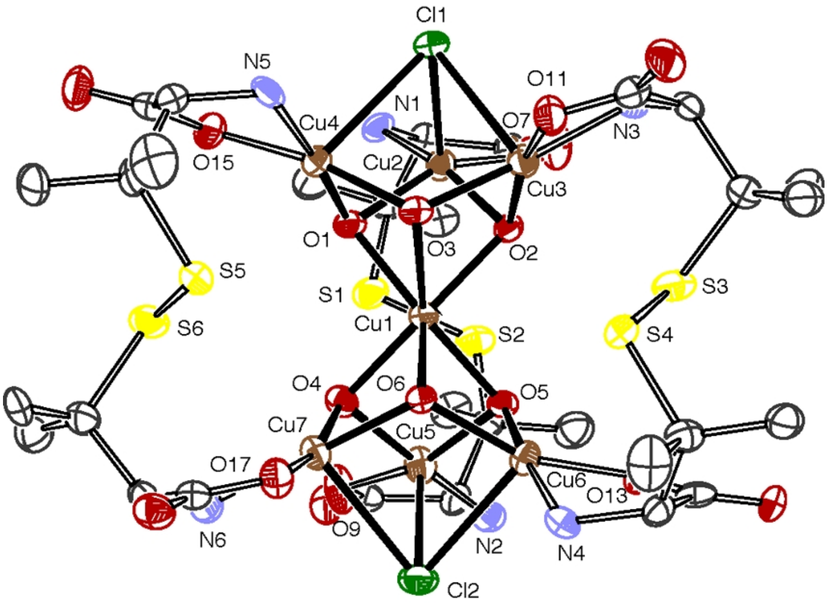

Figure S4. Ortep drawing of **1**. Hydrogen atoms and a disordered copper atom (Cu1B) are omitted for clarity. Cl green, Cu brown, C black, N blue, O red, S yellow. Selected distances [Å] and angles [°]: Cu1–O1 = 1.939(4), Cu1–O2 = 1.979(4), Cu1–O3 = 2.758(5), Cu1–O4 = 1.969(4), Cu1–O5 = 1.963(4), Cu1–O6 = 2.354(5), av $\mathrm{Cu_{outer}}$–$\mathrm{O_{OH}}$ = 1.978(4), av Cu–$\mathrm{O_{D\text{-}pends}}$ = 1.945(5), av Cu–N = 1.977(5), av Cu–Cl = 2.696(2), av Cu···S = 3.314(2), av S–S = 2.031(3), av $\mathrm{Cu_{inner}}$···$\mathrm{Cu_{outer}}$ = 3.084(1), av $\mathrm{Cu_{outer}}$···$\mathrm{Cu_{outer}}$ = 3.279(1), Cu2–Cl1–Cu3 = 76.05(5), Cu2–Cl1–Cu4 = 75.90(5), Cu3–Cl1–Cu4 = 72.57(4), Cu5–Cl2–Cu6 = 75.62(5), Cu5–Cl2–Cu7 = 75.30(5), Cu6–Cl2–Cu7 = 73.75(5), Cu1–O1–Cu4 = 112.7(2), Cu1–O1–Cu2 = 90.27(17), Cu2–O1–Cu4 = 109.41(19), Cu1–O2–Cu2 = 90.80(17), Cu2–O2–Cu3 = 108.76(19), Cu1–O2–Cu3 = 114.9(2), Cu3–O3–Cu4 = 114.6(2), Cu1–O3–Cu3 = 90.19(17), Cu1–O3–Cu4 = 86.13(16), Cu1–O4–Cu5 = 93.11(17), Cu1–O4–Cu7 = 102.47(19), Cu5–O4–Cu7 = 112.5(2), Cu1–O5–Cu6 = 104.06(19), Cu1–O5–Cu5 = 92.16(17), Cu5–O5–Cu6 = 112.0(2), Cu6–O6–Cu7 = 114.9(2), Cu1–O6–Cu7 = 91.39(17), Cu1–O6–Cu6 = 91.46(17).

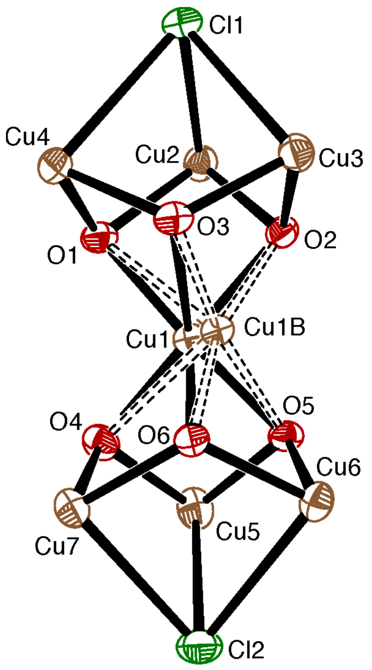

Figure S5. Core structure of **1**. Cl green, Cu brown, O red. Selected distances [Å] and angles [°]: Cu1B–O1 = 2.399(8), Cu1B–O2 = 1.847(8), Cu1B–O3 = 2.107(8), Cu1B–O4 = 2.606(9), Cu1B–O5 = 2.158(8), Cu1B–O6 = 1.851(8), Cu1B–O1–Cu2 = 91.4(2), Cu1B–O1–Cu4 = 91.8(2), Cu1B–O2–Cu2 = 112.8(3), Cu1B–O2–Cu3 = 90.2(3), Cu1B–O3–Cu3 = 85.5(3), Cu1B–O3–Cu4 = 102.2(3), Cu1B–O4–Cu5 = 98.0(2), Cu1B–O4–Cu7 = 85.0(2), Cu1B–O5–Cu5 = 113.2(3), Cu1B–O5–Cu6 = 82.0(2), Cu1B–O6–Cu6 = 90.7(3), Cu1B–O6–Cu7 = 111.5(3).

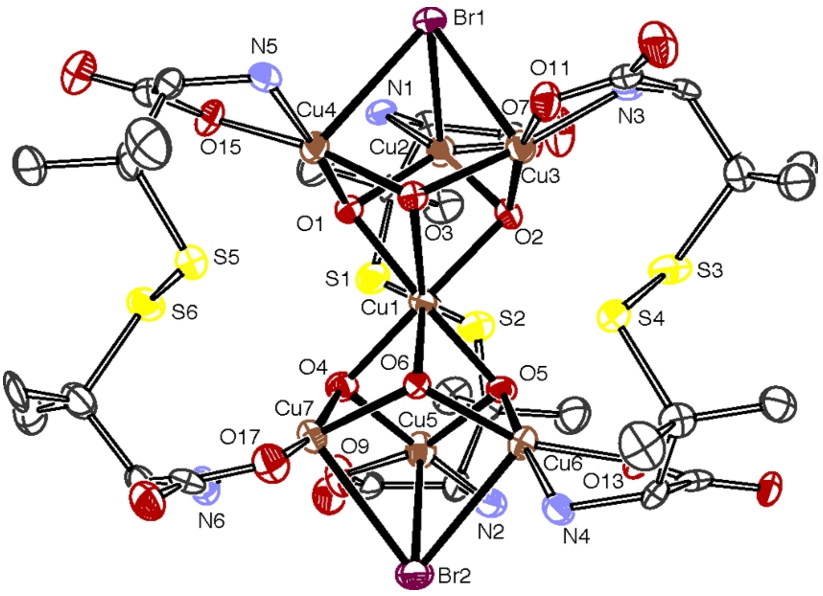

Figure S6. Ortep drawing of **2**. Hydrogen atoms and a disordered copper atom (Cu1B) are omitted for clarity. Br purple, Cu brown, C black, N blue, O red, S yellow. Selected distances [Å] and angles [°]: Cu1–O1 = 1.956(4), Cu1–O2 = 1.986(4), Cu1–O3 = 2.781(5), Cu1–O4 = 1.966(5), Cu1–O5 = 1.952(4), Cu1–O6 = 2.341(5), av $\mathrm{Cu_{outer}}$–$\mathrm{O_{OH}}$ = 1.979(5), av Cu–$\mathrm{O_{D\text{-}pends}}$ = 1.947(5), av Cu–N = 1.973(6), av Cu–Br = 2.823(1), av Cu···S = 3.126(2), av S–S = 2.028(3), av $\mathrm{Cu_{inner}}$···$\mathrm{Cu_{outer}}$ = 3.083(1), av $\mathrm{Cu_{outer}}$···$\mathrm{Cu_{outer}}$ = 3.299(1), Cu2–Br1–Cu3 = 72.63(3), Cu2–Br1–Cu4 = 72.64(3), Cu3–Br1–Cu4 = 69.35(3), Cu5–Br2–Cu7 = 71.60(3), Cu5–Br2–Cu6 = 71.89(3), Cu6–Br2–Cu7 = 70.83(3), Cu1–O1–Cu4 = 112.7(2), Cu1–O1–Cu2 = 89.56(18), Cu2–O1–Cu4 = 110.7(2), Cu1–O2–Cu2 = 90.12(18), Cu2–O2–Cu3 = 108.7(2), Cu1–O2–Cu3 = 114.6(2), Cu3–O3–Cu4 = 114.9(2), Cu1–O3–Cu3 = 89.69(17), Cu1–O3–Cu4 = 85.86(16), Cu1–O4–Cu5 = 93.43(19), Cu5–O4–Cu7 = 113.8(2), Cu1–O4–Cu7 = 102.2(2), Cu1–O5–Cu6 = 104.0(2), Cu1–O5–Cu5 = 92.29(18), Cu5–O5–Cu6 = 113.1(2), Cu6–O6–Cu7 = 116.5(2), Cu1–O6–Cu7 = 91.47(18), Cu1–O6–Cu6 = 91.18(18).

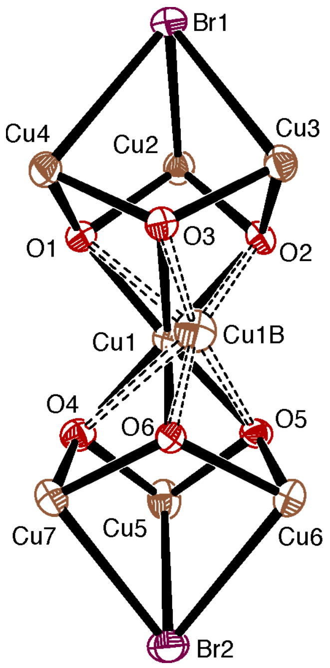

Figure S7. Core structure of **1**. Br purple, Cu brown, O red. Selected distances [Å] and angles [°]: Cu1B–O1 = 2.380(11), Cu1B–O2 = 1.853(11), Cu1B–O3 = 2.127(11), Cu1B–O4 = 2.588(12), Cu1B–O5 = 2.156(11), Cu1B–O6 = 1.855(11), Cu1B–O1–Cu2 = 91.3(3), Cu1B–O1–Cu4 = 91.8(3), Cu1B–O2–Cu2 = 111.0(4), Cu1B–O2–Cu3 = 90.4(4), Cu1B–O3–Cu3 = 85.4(3), Cu1B–O3–Cu4 = 100.9(4), Cu1B–O4–Cu5 = 98.6(3), Cu1B–O4–Cu7 = 85.1(3), Cu1B–O5–Cu5 = 112.9(4), Cu1B–O5–Cu6 = 82.3(3), Cu1B–O6–Cu6 = 90.5(4), Cu1B–O6–Cu7 = 110.9(4).

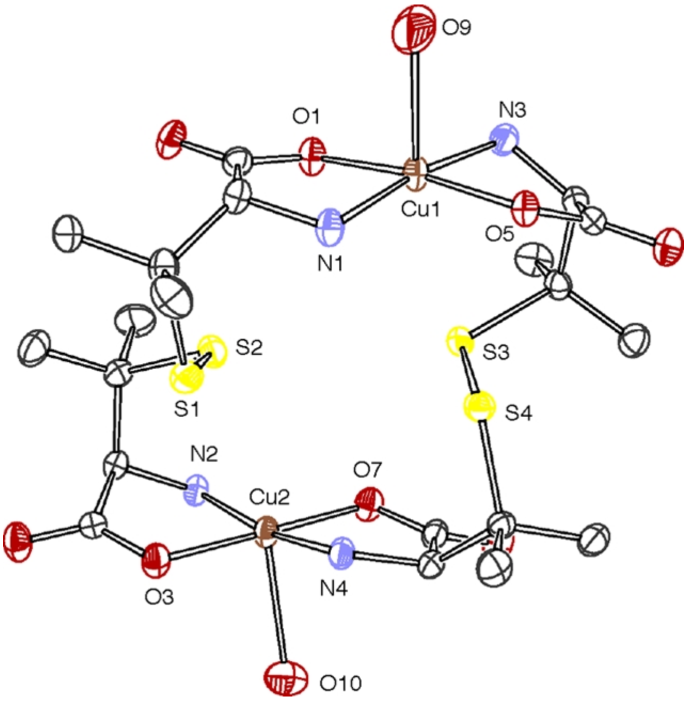

Figure S8. Ortep drawing of **3**. Hydrogen atoms are omitted for clarity. Cu brown, C black, N blue, O red, S yellow. Selected distances [Å]: av Cu–O$_{\text{D-pends}}$ = 1.964(3), av Cu–O$_{\text{water}}$ = 2.382(4), av Cu–N = 1.984(3), av S–S = 2.041(2), Cu···Cu = 6.412(2).

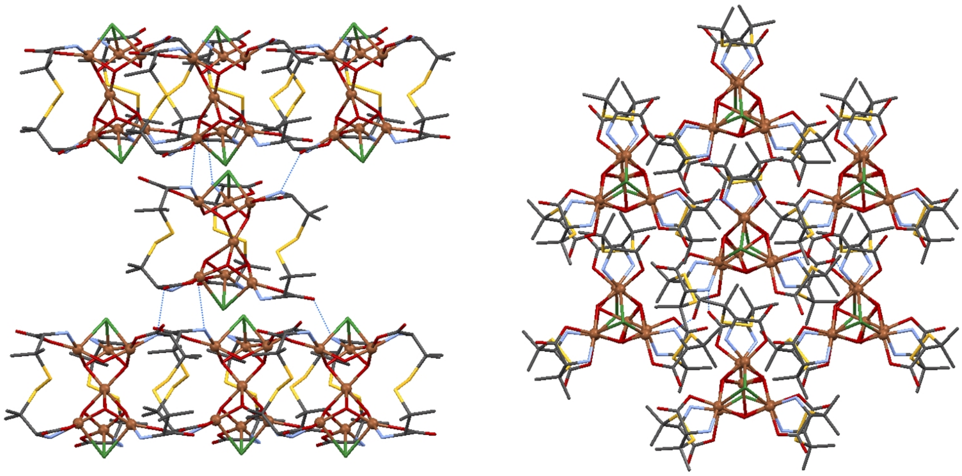

Figure S9. Packing structures of **1**. Blue dashed line represents the hydrogen bonds between carboxyl and amine groups (N···O = 2.852(7) – 2.934(7) Å).

[D] IR Spectra of Complexes.

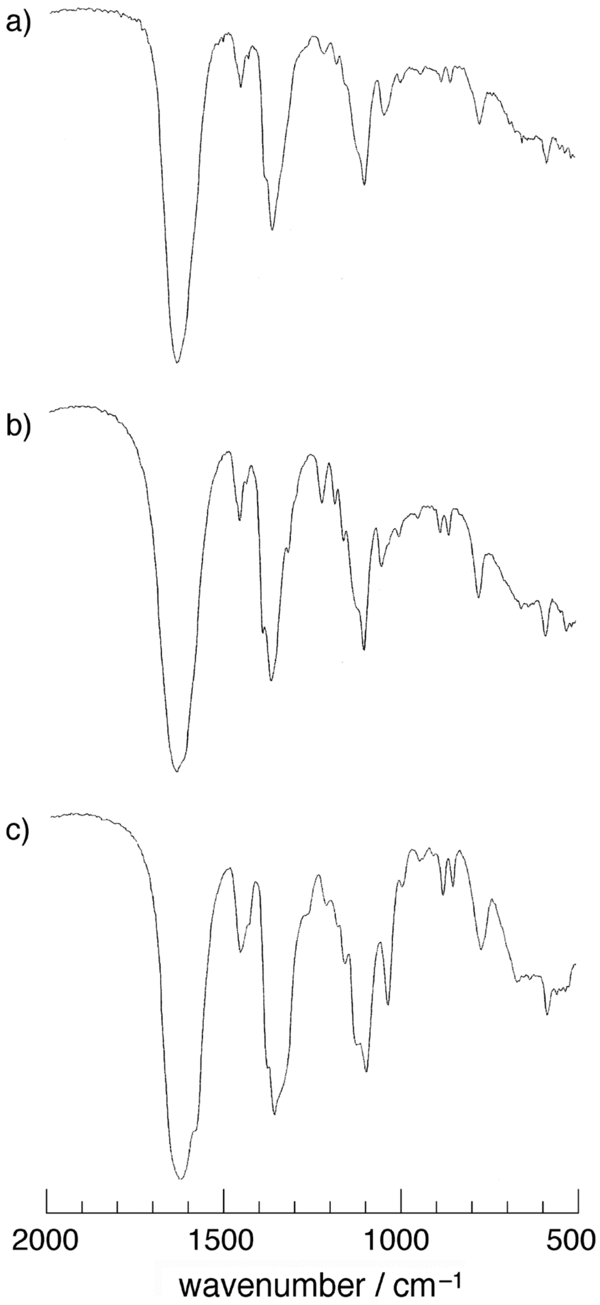

Figure S10. IR spectra of a) **1**, b) **2**, and c) **3**.

[E] Magnetic Data of Complexes.

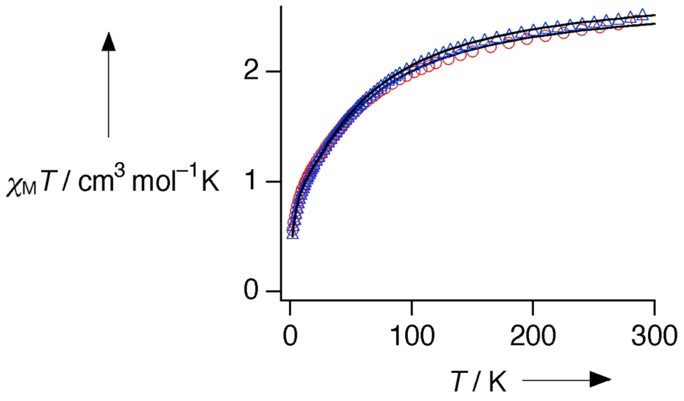

Figure S11. Plots of $\chi_M T$ vs T for **1** (red circle) and **2** (blue triangle). Solid lines correspond to the theoretical curves. Magnetic data were analyzed with the exchange coupling constants J_1, J_2, J_3, and J_4. The parameters obtained from the least-squares calculation are given in the text.

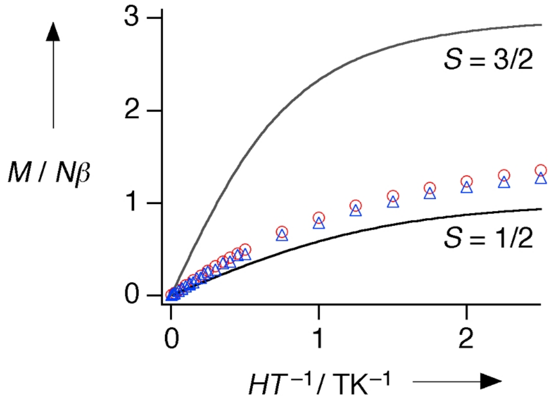

Figure S12. Plots of M vs HT^{-1} for **1** (red circle) and **2** (blue triangle). Solid lines correspond to the theoretical curves (g = 2.0).

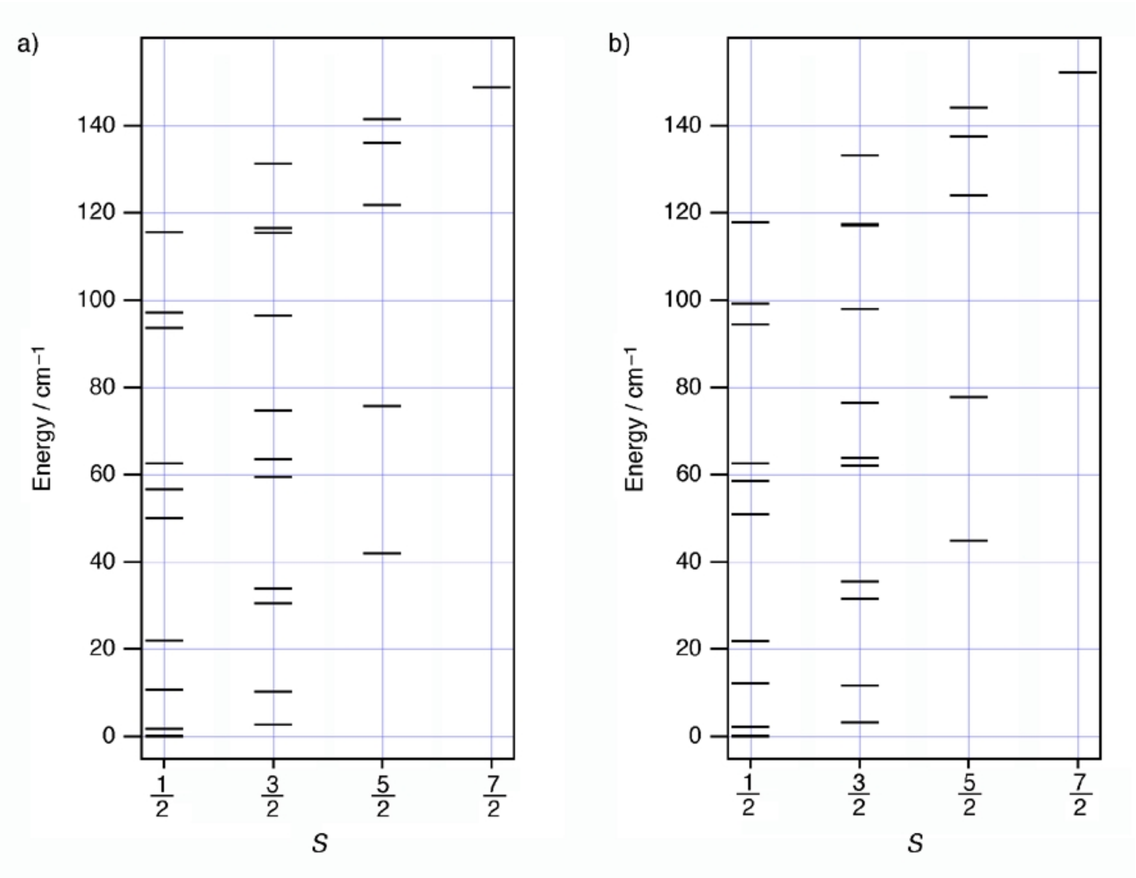

Figure S13. Energy level diagrams of a) **1** and b) **2** using J_1 = –0.9 cm^{-1}, J_2 = –20.9 cm^{-1}, J_3 = –4.1 cm^{-1}, J_4 = –24.0 cm^{-1}, and g = 2.03 for **1** and J_1 = –1.1 cm^{-1}, J_2 = –20.9 cm^{-1}, J_3 = –4.7 cm^{-1}, J_4 = –24.4 cm^{-1}, and g = 2.06 for **2**.