Supporting information for

Crystal Engineering towards Intersecting Channels from a Neutral Network with a bcu-Type Topology**

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**General experimental procedure:**

4-H-ptz was prepared, as described previously in a literature report,\textsuperscript{[12]} other chemicals were purchased commercially and were used as received without further purification. Thermogravimetric analyses were performed under nitrogen with a Perkin–Elmer TGA-7 analyzer. Powder-diffraction measurements were recorded with a Siemens D-5000 diffractometer at 40 kV (30 mA) with Cu-K\(\alpha\) (\(\lambda = 1.5406 \text{ Å}\)), with a step size of 0.02° in \(\theta\) and a scan speed of 1 sec per step size. Variable-temperature dc magnetic susceptibility data were collected for a polycrystalline sample of complex 1 in an applied field of 1.0 kG in the temperature range 2.0–300.0 K with a SQUID magnetometer (Quantum Design, MPMS-7). The sample was embedded in eicosane wax to prevent any torquing of the polycrystalline material in the magnetic field. Pascal’s constants were used to estimate the diamagnetic corrections.

**Detailed Synthesis procedure**

1: A solution of CuCl\(_2\)-2H\(_2\)O (0.10 mmol) and 4-H-ptz (0.13 mmol) in DMF (8 mL) was stirred for 15 min. After allowing the solution to stand at room temperature for several days, deep blue rhombus-like crystals were formed in 61% yield based on 4-H-ptz. The solid product was washed with deionized water and ethanol, and dried in air. A powder X-ray diffraction pattern of the isolated crystals was in good agreement with the pattern simulated from single-crystal data. Elemental analysis. Found: C, 33.59; H, 4.51; N 25.66, (Calcd: C, 33.27; H, 4.31; N, 27.04 on the basis of the formula Cu\(_3\)C\(_{33}\)H\(_{51}\)Cl\(_2\)O\(_3\)N\(_{23}\)O\(_{10}\) \(= [\text{Cu}_3\text{Cl}_2(4\text{-ptz})_4(\text{H}_2\text{O})_2] \cdot 3\text{DMF}\cdot 5\text{H}_2\text{O}\)). These deep blue crystalline solids are insoluble in most common solvents such as water, ethanol, acetonitrile, THF, DMF, acetone, etc. The crystals slowly lose their crystalline properties owing to slow desolvation by guest molecules. Therefore, the open-host polymeric framework of \{[\text{Cu}_3\text{Cl}_2(4\text{-ptz})_4(\text{H}_2\text{O})_2]\}_n in 1 is easily modeled from the X-ray structure analysis, but the guest molecules cannot be accurately located owing to their positional disorder. A TG analysis was carried out to characterize the content of guest molecules. A TG analysis of 1 revealed a weight lost of 26% after
heating to 220 °C, corresponding to the loss of 3 mol of DMF and 5 mol of H₂O per formula unit. Thus, Compound 1 was formulated as \([\text{Cu}_3\text{Cl}_2(4\text{-ptz})(\text{H}_2\text{O})_2] \cdot 3\text{DMF} \cdot 5\text{H}_2\text{O}\)ₙ, which is further supported by the elemental microanalysis results.

**Magnetic Studies**

The magnetic behavior of complex 1 is shown in Figure S1 in the form of inverse magnetic susceptibilities (1/\(\chi_M\)) and \(\chi T\) vs. temperature plots, \(\chi_M\) being the molar magnetic susceptibility per copper. The value of \(\chi_M T\) is 0.448 cm³ K mol⁻¹ at 300 K, which is approximately the value expected for a single uncoupled Cu²⁺ ion. The value of \(\chi T\) decreases slowly with decreasing temperature up to 30 K and sharply below 20 K, reaching a value of 0.189 cm³ K mol⁻¹ at 2.0 K. This behavior is characteristic of compounds with an overall antiferromagnetic interaction between the copper ions.

A qualitative analysis of the magnitude of the antiferromagnetic was made based on the Curie-Weiss expression,[⁵¹] 1/\(\chi_M\) = (T−\(\theta\))/\(C_M\), yielding a Curie constant \(C_M\) of 0.450 cm³ K mol⁻¹ and a Weiss’s constant \(\theta\) of −6.02 K. The negative \(\theta\) value indicates the weakly antiferromagnetic coupling via the tetrazole moiety of 4-ptz and chloride bridging ligands within the copper metal centers.

The magnetic data were interpreted using the expression for the molar magnetic susceptibility of a linear trinuclear system with \(S = 1/2\),[⁵²] which was based on the phenomenological spin Hamiltonian with quantum spin operators \(S_{Cu1}\), \(S_{Cu2}\) and \(S_{Cu2A}\) where Cu1, Cu2 and Cu2A refer to nearest neighbor ions:

\[
H = -2J \left( S_{Cu1} \cdot S_{Cu2} + S_{Cu1} \cdot S_{Cu2A} \right) - 2J' \left( S_{Cu2} \cdot S_{Cu2A} \right)
\]

where \(J\) is the exchange integral between the central and terminal copper ions \((J = J_{12} = J_{12A})\) and \(J'\) is the exchange integral between the terminal copper ions \((J' = J_{22A})\). The magnetic susceptibility is given by

\[
\chi_M = \frac{Ng^2 \beta^2}{4kT} \left[ \frac{\exp(-2J / kT) + \exp(-2J' / kT) + 10 \exp(J / kT)}{\exp(-2J / kT) + \exp(-2J' / kT) + 2 \exp(J / kT)} \right]
\]  

(1)
In Equation 1, the terms $N, k, ?$ and $T$ have their usual meanings. The $g$ values for all three copper atoms are assumed to be equal. The assumption of negligible magnetic exchange between the terminal Cu ions is justified in view of the study of triply N,N′-1,2,4-triazole bridged $[\text{Fe}_3(\text{hyetra})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ and $[\text{Co}_3(\text{dat})_6(\text{datH})_2(\text{H}_2\text{O})_6]\text{Cl}_3$ trinuclear clusters, where the central metal ion is diamagnetic and no magnetic interactions could be detected between the paramagnetic terminal metal ions. The magnetic susceptibility data were fitted by

$$
\chi_M = \left[ \frac{Ng^2}{4kT} \right] \left[ \frac{1 + \exp(-2J / kT) + 10 \exp(J / kT)}{1 + \exp(-2J / kT) + 2 \exp(J / kT)} \right] \tag{2}
$$

The resulting best fit with $J' = 0$ is shown as a solid line in Figure 8, with $g = 2.12$, and $J = -2.84 \, \text{cm}^{-1}$. The observed antiferromagnetic interaction is resolved into contributions arising from each Cu–ligand–Cu linkage. The main parameters are: the distance between the copper atoms and Cu–ligand–Cu angle, the extent of planarity of the bridging network, as well as the nature of the bridging ligand. The apical Cl bridging the Cu(1) and Cu(2) atoms, is considered to be orthogonal in a magnetic sense ($\angle \text{Cu–Cl–Cu} = 84.46^\circ$) and so would likely contribute little to the antiferromagnetic exchange process. The propagation of antiferromagnetic exchange interactions in the linear Cu$_3$ unit would be expected to depend predominantly on the 4-ptz bridges and may be processed via the d$_{x^2-y^2}$ orbitals on the Cu$^{II}$ ions which interact with the s orbital of the nitrogen atoms of the tetrazolate ligands, which are all situated in the equatorial plane and contain Cu–N–N–Cu torsion angles of $-3.41^\circ$. The propagation of the antiferromagnetic exchange coupling significantly decreased in this two tetrazole and one chloride bridged tricopper ($J = -2.84 \, \text{cm}^{-1}$) compared with those bridged by two triazole and one chloride ($J = -37.6 \, \text{cm}^{-1}$ and $J = -16.9 \, \text{cm}^{-1}$)\footnote{[s5,s6]}. This antiferromagnetic coupling via the tetrazole ligand will be very weak, although Cu–N–N–Cu torsion angles of $-3.41^\circ$ having short Cu–N distances would increase the antiferromagnetic coupling. By crystal engineering of the substitute on the 4-pyridyl, increasing the
Cu–N–N–Cu torsion angles in tricopper center would change the exchange coupling from antiferromagnetic to ferromagnetic.[s7]

Figure S1. Plots of inverse magnetic susceptibilities (1/$\chi_M$) and $\gamma_M T$ per mole of copper versus temperature; the solid line of the inverse magnetic susceptibilities is from the fitting results of Curie-Weiss law and the solid line of $\gamma_M T$ is from the fitting results of the trinuclear magnetic equation.

** References of magnetic studies. 


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