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Coordination Polymers

A Bistable Porous Coordination Polymer with a Bond-Switching Mechanism Showing Reversible Structural and Functional Transformations**

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In recent years, porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) with flexible structures have attracted considerable attention, owing to their potential as functional materials.[1] Unlike rigid frameworks, where, in most cases, structure and properties remain unchanged after removal of guest molecules, flexible frameworks are very sensitive to the presence of guests and undergo structural variations depending upon the amount and nature of the guest molecules inside the framework.[2] Such compounds are capable of forming bistable phases and are expected to exhibit not only structural variations but also modulation of their physical properties, such as chirality as well as optical and magnetic behavior, to achieve multiple functions that are not observed in robust frameworks or other conventional solids. Structural flexibility has also been observed in inorganic frameworks, although the detected changes are not as drastic as those of PCPs. To create such systems, we have focused on modulation of the crystal structure by reversible removal of guest molecules, to produce multifunctional bistable coordination polymers. If the host framework undergoes single-crystal-to-single-crystal (SCSC) transformations,[3] crystallographic analysis is a very useful tool for deepening our understanding of the dynamic behavior, and correlating the bistable structures with physical properties, such as magnetism.[1d,4] PCPs containing flexible ligands and metal ions with variable coordination numbers have great potential for this purpose, as such flexibility allows for stability in various structural forms.

Porous crystals based on 2D frameworks have several useful characteristics with regard to dynamic guest-responsive phenomena: 1) interlayer separations, which play a major role in guest-inclusion; 2) framework flexibility, as a result of sliding of the 2D layers and closing/opening of the channel spaces by the guest molecules; 3) rearrangement of the frameworks by cleavage and formation of coordination bonds between the layers, leading to expansion/shrinkage of the 2D layered structures by the guest molecules. Most importantly, the transformation between the 2D and 3D frameworks, with cleavage and generation of new bonds, is expected to lead to large differences in their structural and functional behaviors. These unique materials have a high potential for realizing new functions, such as switching and sensing. To make bistable compounds with drastic structural differences, 2D frameworks containing a flexible ligand and a metal ion with variable coordination numbers may easily undergo transformation to a 3D structure upon guest removal by contracting/expanding and concurrent sliding of the 2D layers, using the bond-switching mechanism of the coordination bonds around the metal centers (Figure 1).[5–8]

In this regard, the Cu^{II} metal ion is very promising, as it has versatile coordination chemistry and can readily adopt octahedral, square-pyramidal, trigonal bipyramidal, and square-planar geometries. Herein we report a 2D coordination polymer $\{[Cu_2(tci)(OH)(H_2O)_3]\cdot 1.5\,H_2O\}_n$ (**1**, tci = tris(2-carboxyethyl)isocyanurate), consisting of a Cu^{II} ion and a flexible ligand (tci) that, upon guest removal, transforms into a 3D framework by sliding of the 2D sheets and contracting of the spaces between the layers, as indicated by reversible SCSC transformations. The versatile coordination geometry of the Cu^{II} ion and ligand flexibility play key roles in the reversible structural transformations by cleavage and generation of coordination bonds. These reversible structural transformations are accompanied by changes in physical properties, such as optical and magnetic behavior. The dry phase of **1** can absorb H_2O molecules, but rejects organic solvents, such as methanol, ethanol, acetone, and tetrahydrofuran.

The 2D framework $\{[Cu_2(tci)(OH)(H_2O)_3]\cdot 1.5\,H_2O\}_n$ (**1**) was synthesized by the reaction of $Cu(NO_3)_2\cdot 6\,H_2O$ and tris(2-carboxyethyl)isocyanurate in aqueous KOH solution, affording a greenish-blue crystalline product. The crystal structure of **1** was determined by single-crystal X-ray diffraction, as shown in Figure 2A,C and Figure S1 in the Supporting Information. There are three crystallographically independent hexacoordinated Cu^{II} ions (Cu1–Cu3) with two different coordination environments (Cu2 and Cu3 have similar

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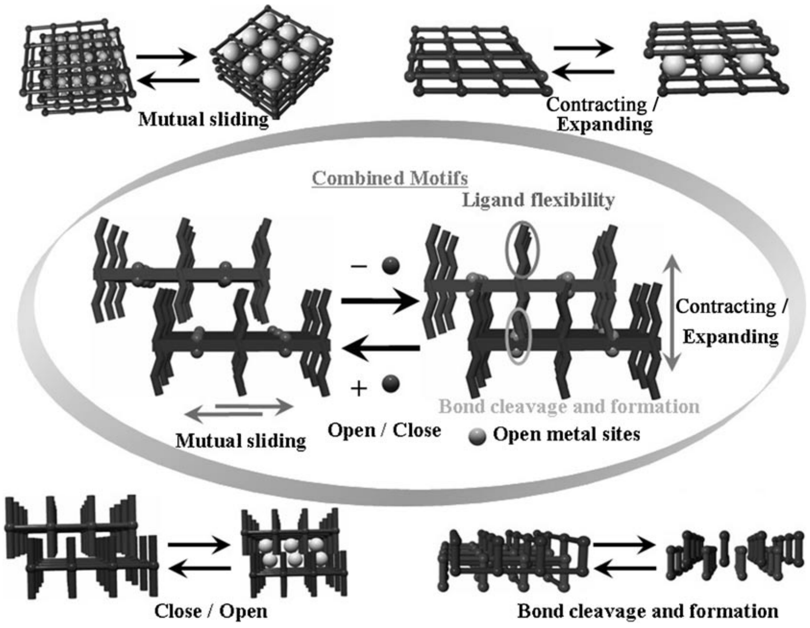

Figure 1. Schematic representation of fundamental motifs observed for dynamic guest sorption involving 2D coordination frameworks (outside circle) and a model of combined motifs (inside circle).

environments) in the asymmetric unit. The three Cu^{II} ions are all bridged by the μ_3 oxygen atom (O10) of the hydroxy anion. Cu1 is also bridged to Cu2 and Cu3 through water molecules (O_w2 and O_w3) and by the carboxylate groups of the ligand. A linear chain is formed by Cu2–O10–Cu3 linkages with Cu1 atoms located alternately on opposing sides of the chain. The distances between the copper centers are: Cu1–Cu2 3.220(2) Å, Cu1–Cu3 3.057(1) Å, and Cu2–Cu3 3.760(1) Å. The hydroxo-bridged Cu^{II} chains form linearly, with both Cu2 and Cu3 in central symmetry positions. The sixth coordination site on Cu1 is occupied by one coordinated H_2O molecule. Adjacent Cu^{II} chains, within the same 2D sheet structure, are bridged by two of the three symmetrical carboxylate groups of the ligand. The oxygen atoms of the third carboxylate group (O4 and O5) form hydrogen bonds with two bridging H_2O molecules (O_w2 and O_w3) and the singly coordinated H_2O molecule (O_w1) within the next layer. Notably, the free carboxylate anionic oxygen centers form very strong H bonds (with lengths of 2.592–2.653 Å) with the coordinated and bridging H_2O molecules (O_w1–O_w3), compared with the H bonding between O_w2 and the neutral oxygen atom O1 of the central ring of tci (2.977 Å). There is also the possibility of charge distribution between the free carboxylate oxygen centers and H_2O molecules. Free H_2O molecules (O_w4 and O_w5) are present in the channels of the 2D layers.

The powder X-ray diffraction (PXRD) pattern of the as-synthesized bulk compound (**1**) matched with the simulated pattern, indicating phase purity, which is also supported by elemental analysis. The thermogravimetric analysis (TGA) curve of **1** indicates desorption of all water molecules (approximately 14.3 %) at temperatures below 100 °C, which corresponds to 4.5 H_2O molecules per formula unit (14.27 %).

The dehydrated phase (**1a**) was generated by heating **1** 125 °C to remove the water molecules completely, which was confirmed by TGA (see the Supporting Information, Figure S2). The color of the compound changed from greenish-blue for **1** to deep blue for **1a**. The PXRD pattern of**1a** is different from that of the as-synthesized phase **1**, but maintains crystallinity, indicating that a large structural transformation occurred upon dehydration. However, when the dehydrated phase was exposed to air, it immediately started to change, as could be seen from the change in color. Within two days, a complete color change, to that of **1**, had occurred, indicating reversibility of the structural transformation. This reversibility is also supported by the PXRD and TGA results. The rehydrated phase (**1r**) gave a similar PXRD pattern to the as-synthesized phase (**1**), and the TGA curve also indicated a similar amount of water-release as for the as-synthesized compound.

To characterize the dehydrated phase by single-crystal X-ray diffraction we heated the as-synthesized greenish-blue crystal at 80 °C for 4 hours until the color of the crystal had changed to deep blue, and then collected data at that temperature. Data collection was performed at an elevated temperature as, upon lowering the temperature, even under a nitrogen atmosphere, the dehydrated compound takes up any available moisture as a result of a high affinity toward water. Structure determination (Figure 2) revealed that, upon dehydration, the 2D structure had transformed to a 3D framework $\{[Cu_2(tci)(OH)]_2\}_n$ (**1a**). Several SCSC structural transformations have been reported in which, upon removal of the guest molecules, dimensionality of the structure has been changed[3c,g,i] but structural transformations between 2D and 3D are very rare.[4c,8] In the asymmetric unit of **1a**, there are two similar but crystallographically distinct trinuclear Cu^{II} repeating units, compared to one in compound **1**, with a change in the crystallographic point group, from monoclinic to triclinic, owing to the new coordination bonds formed by the free carboxylate groups with the trinuclear Cu^{II} unit of the next layer. The coordination environment around the metal centers is changed significantly. Most importantly, all of the Cu^{II} centers are changed from hexadentate octahedral to tetradentate square planar (Figure 2D). Bridging and coordinated water molecules from Cu^{II} centers have been removed and the hydroxy bridge between Cu2 and Cu3 is cleaved. The tridentate central hydroxo bridge between the three Cu^{II} centers is transformed to a bidentate bridging ligand between Cu1 and Cu3, isolating Cu2 in terms of direct bridging by a single atom. Two Cu1 and one Cu3 make a discrete trinuclear unit, whereas in compound **1** all three Cu^{II} ions formed a hydroxo-bridged chain. In **1a**, the free carboxylate oxygen centers (O4 and O5) of one 2D sheet are coordinated to Cu1 and Cu2 of the adjacent sheets on both sides, leading to the transformation of the 2D sheets to

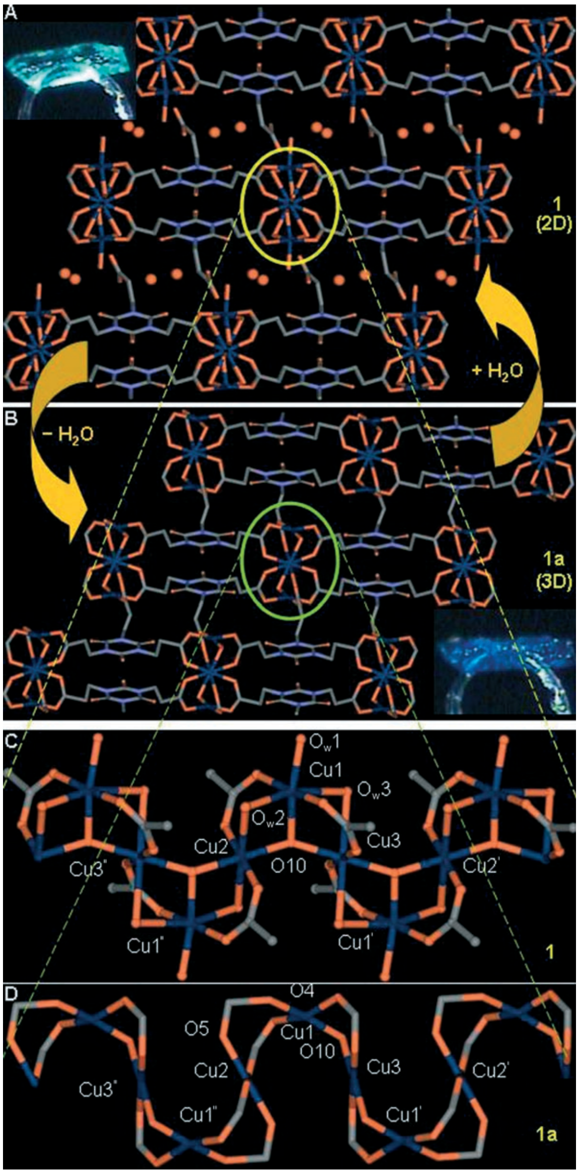

Figure 2. Perspective views of the structure and bonding environment of the as-synthesized compound **1** (A and C) and, after guest removal, dehydrated structure **1a** (B and D). Insets show the picture of the corresponding repeating units. C gray, N sky blue, O light orange, Cu deep blue.

the 3D framework. From Figure 2A we can see that the 2D sheets are not in a perfect position to form the 3D framework. Sliding of the sheets and contracting of spaces are necessary to coordinate the free carboxylate groups of one 2D sheet to the nearest Cu^{II} center of the adjacent sheets. The shortest distance between the free carboxylate oxygen atom of one layer and the Cu^{II} center of the next layer was 3.810(2) Å, which was the minimum mutual movements necessary to make the 3D structure. PXRD patterns of **1a**, generated at variable temperatures under vacuum, matched well with the simulated pattern (see the Supporting Information, Figure S4). To test the reversibility of the transformation, dehydrated crystals were kept in the open air for a few days and when the color of the crystal completely transformed from deep blue to the greenish-blue of the original sample, crystallography was carried out and the crystals of **1r** were seen to match with compound **1**, indicating that the transformation is completely reversible.

In the dehydrated compound **1a**, all of the Cu^{II} sites have four-coordinate square-planar geometry, which means that it has unsaturated open metal sites and should have a strong affinity to guest molecules at the so-called guest-accessible metal sites. In a typical experiment, the dehydrated compound was exposed to dry solvents. After two days, the compound was analyzed by TGA and XRPD. Interestingly, the TGA data indicated no uptake of any common organic solvents, such as methanol, ethanol, tetrahydrofuran, and acetone. These results are also supported by the lack of change in the XRPD pattern after solvent treatment of the dehydrated sample. However, as discussed previously, the compound has a strong affinity for water molecules. This selectivity may arise from the hydrophilicity of the framework, because of the carbonyl groups of the ligand, and also the narrow channel area to access the metal centers. The above results were also supported by the sorption measurements. The dehydrated phase **1a** absorbed nearly 4.5 molecules of water per formula unit, which is similar to the amount of water present in the as-synthesized phase **1** (Figure 3a).

To test the modulation of physical properties by structural transformations, the optical and cryomagnetic properties of **1** and **1a** were investigated. Compound **1** turned from greenish-blue to dark blue upon dehydration (**1a**), this change being

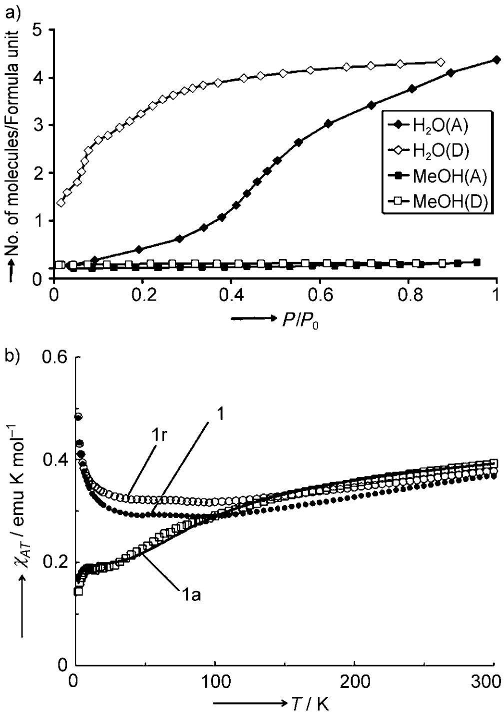

Figure 3. a) Absorption (A) and desorption(D) profiles of H_2O and MeOH at 298 K for **1a**. b) The $\chi_A T$ versus T plots for as-synthesized compound **1** (●), dehydrated phase **1a** (□), and rehydrated sample **1r** (○) under a 500 Oe field. The solid line represents the curve calculated for **1a** using Equation (1).

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associated with the change in the coordination geometry around the Cu^{II} ions from a six-coordinate octahedral geometry in **1** to a four-coordinate square-planar geometry in **1a**. The visible reflectance spectrum for **1** shows an absorption band at around 790 nm (A band), in contrast to the two different absorption bands at around 610 nm (C band) and 700 nm (B band) for **1a** (see the Supporting Information, Figure S5) .

The magnetic properties of **1** and **1a** are significantly different. The $\chi_A T$ versus T plots and the magnetization curves of **1**, **1a**, and the rehydrated phase (**1r**) are shown in Figure 3b and Figure S6 in the Supporting Information. The $\chi_A T$ value of **1** is 0.368 emu K mol^{-1} at 300 K which agrees well with the spin-only value (0.375 emu K mol^{-1}) expected for one magnetically isolated Cu^{II} ($S = 1/2$) ion. The $\chi_A T$ value decreased gradually with decreasing temperature to approximately 30 K, then increased more sharply below this temperature. A plot of $\chi_A{}^{-1}$ versus T in the temperature ranges of 300–150 K obeys the Curie–Weiss law ($\chi_A = C/(T+q)$) with a Weiss constant $\theta = -84$ K. As shown in Figure 2C, O10 forms a μ_3 bridge between Cu1, Cu2, and Cu3, resembling a spin-frustrated triangle core, where the bridging angles of Cu1-O10-Cu2, Cu1-O10-Cu3, and Cu2-O10-Cu3 are 101.26°, 107.00°, and 146.67°, respectively. In this structure, antiferromagnetic interactions in the Cu2-O10-Cu3 chain are much stronger than those between Cu1 and Cu2/Cu3.[4l] From a structural aspect, the decrease in the $\chi_A T$ value in the high-temperature region is attributed to the dominant antiferromagnetic interaction in the 1D Cu2-O10-Cu3 chain. The successive increase in the $\chi_A T$ value below 100 K suggests the pendant Cu1 centers interact ferromagnetically through the antiferromagnetically coupled 1D chain in a spin canting fashion (see Supporting Information, Scheme S1). The sample was subsequently heated to 400 K in the SQUID (superconducting quantum interference device) with helium substitution for in situ dehydration of **1**. The dehydrated form **1a** exhibits significantly different magnetic behavior from **1.** The $\chi_A T$ value gradually decreased with decreasing temperature and became virtually constant below 30 K. The Weiss constant was estimated to be −63 K in the temperature range of 300–100 K. The structure can be separated magnetically into the two parts, a μ_2-oxo- and *syn-syn*-carboxylato-bridged Cu1-Cu3-Cu1′ trinuclear unit, and a Cu2 mononuclear unit bound to Cu1 through two *syn-syn*-carboxylato-bridges. The magnetic behavior was analyzed using Equation (1):

$$\chi_A = \frac{3Ng^2\beta^2}{48k(T-\theta)}\,\frac{1+\exp(2J/kT)+10\exp(3J/kT)}{1+\exp(2J/kT)+2\exp(3J/kT)} + \frac{Ng^2\beta^2}{16kT} \qquad (1)$$

based on the {trinuclear + mononuclear} model using the spin Hamiltonian, $\mathcal{H} = -J(S_{Cu1}S_{Cu3} + S_{Cu1'}S_{Cu3})$, where N is Avogadro's number, β is the Bohr magneton, k is the Boltzmann constant, J is the exchange integral, θ is the Weiss term including magnetic interaction between trinuclear and mononuclear units, and $N\alpha$ is temperature-independent paramagnetism.[9] The magnetic behavior was well-simulated with $J = -43$ cm^{-1}, $g = 2.10$, $\theta = -0.5$ K, and $N\alpha = 1.0 \times 10^{-4}$ emu mol^{-1}, which demonstrates the antiferromagnetic interaction between Cu1 and Cu3, and the weak antiferromagnetic interaction between the Cu1-Cu3-Cu1′ unit and Cu2 (see the Supporting Information, Scheme S1). In the case of **1a**, the dehydration process increased its structural dimensionality (2D to 3D) with fragmentation of its magnetic exchange pathways, resulting in the weakening of its magnetic correlation, and consequently exhibiting the opposite trend to previously reported related compounds.[4d–g] Notably, the initial approximate magnetic behavior of **1** was recovered after hydration of **1a**, which is highly associated with the structural reversibility. The magnetization curves of **1**, **1a**, and **1r** also support the reversible magnetic changes (see the Supporting Information, Figure S6).

In conclusion we have synthesized a dynamic guest-responsive coordination polymer of Cu^{II} using a highly flexible ligand. The as-synthesized 2D framework compound underwent a reversible SCSC structural transformation to a 3D framework upon dehydration and rehydration, associated with the mutual sliding of the 2D sheets and contracting of the framework. This structural bistability also results in drastic changes in the optical and magnetic properties. The compound shows a color change from greenish-blue to deep blue. Consequently, there is a significant shift and the appearance of a new band in the reflectance spectrum. The magnetic behavior was reversibly changed by hydration and dehydration, accompanied by the structural transformation. Reversibility of the transformation has also been demonstrated by the single-crystal X-ray diffraction, TGA, and PXRD measurements. The framework had a strong affinity for H_2O molecules but rejected common organic solvents, such as MeOH, EtOH, THF, and Me_2CO.

Experimental Section

Synthesis of $\{[Cu_2(tci)(OH)(H_2O)_3]\cdot 1.5\,H_2O\}_n$ (**1**): $Cu(NO_3)_2\cdot 6\,H_2O$ (0.24 g; 1 mmol) was added to a solution of tris(2-carboxyethyl)isocyanurate (1 mmol) in H_2O (25 mL) Excess aqueous KOH solution was added until a precipitate started to form. After removing undissolved matter by filtration, the solvent was allowed to evaporate slowly at room temperature, whereupon, after 10 days, **1** appeared as greenish-blue rectangular parallelepiped crystals in 45 % yield. Elemental analysis calcd (%) for $C_{12}H_{22}N_3O_{14.50}Cu_2$: C 25.40, H 3.90, N 7.40 %; found: C 25.60, H 4.11, N 7.39 %.

Physical measurements: X-ray powder diffraction measurements were carried out on a Rigaku RINT-2000 Ultima diffractometer with Cu Kα radiation. Thermogravimetric analyses were recorded on a Rigaku Thermo plus TGA 8120 apparatus in the temperature range 300–800 K under a nitrogen atmosphere at a heating rate of 1 K min^{-1}. The absorption isotherms of H_2O and other solvents were measured at 298 K with BELSORP18 volumetric adsorption equipment from Bel Japan. The anhydrous sample $\{[Cu_2(tci)(OH)]_2\}_n$ (**1a**) was obtained by heating at 400 K under reduced pressure (<10^{-2} Pa) for more than 10 h. Magnetic measurements were carried out on a Quantum Design MPMS-XL5R SQUID susceptometer. Samples were loaded into gelatin capsules, mounted inside a straw, and fixed to the sample transport rod. Diamagnetic correction was made using Pascal's constants. The magnetic susceptibility per Cu atom χ_A was corrected for the diamagnetism of the constituent atoms. DC magnetic measurements were performed in the temperature range 2–300 K in an applied DC field of 500 Oe. Field dependences of magnetization were measured in the field range 0–50 kOe at 2 K.

X-ray crystal structure analysis: Single-crystal X-ray data collection was carried out on a Rigaku mercury diffractometer with a

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graphite monochromated $Mo_{K\alpha}$ radiation ($\gamma = 0.71069$ Å) and a CCD detector. The structure was solved by direct methods using SHELXTL[10a] and was refined on F^2 by full-matrix least-squares technique using SHELXL-97.[10b] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms except those on water molecules were positioned geometrically, and treated as riding atoms using SHELXL default parameters. Disordered solvents were refined isotropically, whereas other non-hydrogen atoms were refined anisotropically. Crystal data for **1**: Formula $C_{12}H_{22}N_3O_{14.5}Cu_2$, monoclinic, space group $P2_1/n$, $a = 13.339(3)$, $b = 7.519(2)$, $c = 20.096(4)$ Å, $\beta = 99.96(3)°$, $V = 1985.1(7)$ Å^3, $Z = 4$, $T = 213(2)$ K, $R = 0.0708$, $wR_2 = 0.2209$, GOF = 1.092. Crystal data for **1a**: Formula $C_{24}H_{26}N_6O_{20}Cu_4$, triclinic, space group $P\bar{1}$, $a = 8.113(3)$, $b = 10.649(2)$, $c = 19.590(5)$ Å, $\alpha = 76.830(6)$, $\beta = 88.480(5)°$, $\gamma = 88.620(3)$, $V = 1647.1(9)$ Å^3, $Z = 2$, $T = 353(2)$ K, $R = 0.1947$, $wR_2 = 0.4657$, GOF = 1.349. CCDC 691369 (**1**), and CCDC 691368 (**1a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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