Unprecedented Marriage of a Cationic Pentanuclear Cluster and a 2D Polymeric Anionic Layer Based on a Flexible Tripodal Ligand and a Cu$^{II}$ Ion

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The anionic CdI$_2$-type topological net, [Cu$_2$(tci)$_2$(OH)$_2$]$_2$[tci$^-$][Cu$_2$(tci)$_2$(OH)$_2$]$_2$[H$_2$O]$_8$[$\mu$-tris-(2-carboxyethyl)isocyanurate] forms a complementary 3D supramolecular framework. Interestingly, there exist centrosymmetric cyclic (H$_2$O)$_{16}$ clusters in the cavities.

Metal–organic coordination polymers have recently attracted great interest not only because of their versatile intriguing architectures and topologies but also because of their potential applications as functional materials.1,2 The prediction of coordination frameworks is still subjective and cannot be generalized because the self-assembly process is highly influenced by several factors,3 such as the metal/ligand nature, solvent, templates, and counterions. As good candidates for rigid tripodals in the construction of metal–organic coordination polymers, 1,3,5-tris(4-carboxyphenyl)benzene and 1,3,5-benzenetricarboxylic acid have been relatively well-known and have shown interesting coordination architectures.4 However, as a flexible tripodal ligand with highly flexible arms, tris(2-carboxyethyl)-isocyanurate (H$_3$-tci), has not been well-explored to date, although several references have been documented.5 Herein, we report a novel compound self-assembled by copper acetate and the H$_3$-tci ligand, namely, [Cu$_2$(tci)$_2$(OH)$_2$]$_2$[Cu$_2$(tci)$_2$H$_2$O]$_8$[Cu$_2$(tci)$_2$]$_2$[H$_2$O]$_{18}$ (I). This compound is interesting for several reasons: (i) the anionic portion of the structure forms a noninterpenetrated CdI$_2$-type layer not observed with Cu$^{II}$ and simple anions; (ii) the formation of the CdI$_2$-type anionic layer is enabled by charge compensation via a complex cation, rare for a coordination solid;6 (iii) the compound’s counterpoint itself is a pentanuclear copper(II) cluster, which is stabilized by incorporation as part of the iron pair; (iv) in the cavities of this host–guest compound, there exist rare cyclic (H$_2$O)$_{18}$ clusters. This is an unusual example of molecular recognition and a mutual structural stabilization effect in a coordination framework.


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one μ3-OH group, four aqua ligands, and five and a half lattice water molecules. In the pentanuclear copper cluster motif, two and a half crystallographically independent CuII centers that exhibit two different coordination polyhedra are connected by two tci ligands to form a pentanuclear copper cluster (Figure 1a). The Cu2 atom lies on the inversion center and is coordinated by six oxygen atoms from two μ3-OH groups and four carboxylate oxygen atoms of four individual tci ligands. Cu3 and Cu4 have the same coordination polyhedra, which are coordinated by five oxygen atoms from two tci ligands. Cu3 -OH groups (Figure 1b), in which the five copper centers are all coplanar and arranged in two symmetric Δ-type patterns (Cu2...Cu3 3.102 Å; Cu2...Cu4 3.256 Å; Cu3...Cu4 3.461 Å). The tci ligand adopts a pentadentate coordination mode in which each carboxylate group bridges two copper centers in a syn,syn mode and has the cis,cis,cis conformation with up and down orientations alternatively. In the 2D layer moiety, there is only one crystallographically independent CuII center. As shown in Figure 1c, the Cu1 center is coordinated by five oxygen atoms from five carboxylate groups of five individual tci ligands, displaying a distorted tetragonal-pyramid geometry. The tci ligand also adopts a pentadentate coordination mode, of which two carboxylate groups take the same syn,syn coordination mode, while the third carboxylate group bridges one CuII center in a monodentate fashion (Figure 1d). Four carboxylate groups with syn,syn coordination modes bridge two adjacent copper centers to form paddlewheel metal clusters. Unlike the pentanuclear copper cluster, the tci ligand in the 2D layer has the cis,trans,trans,trans conformation. The energy barrier between the cis,cis,cis and cis,trans,trans,trans conformers is very small and can be easily overcome. The conformation of the ligand is probably dominated by the cluster formation or sometimes packing forces.

An interesting structural feature in I is that the 2D layer can be rationalized as a noninterpenetrating CdI2-type network by simplifying the tci ligand as a 3-connecting node (vertex symbol 4) and the CuII -CuII dimer as a 6-connecting node (vertex symbol 468) (Figure 2). The intrinsic factor that prevents interpenetration in this network may be attributed to the presence of pentanuclear copper clusters between the 2D layers. The CdI2-type network, which can be represented by Wells notation {4}31, is one of the Catalan nets known in inorganic compounds such as metal alkoxides and hydroxides.9 The main topological character of the CdI2 net is that it can be regarded to form by the offset overlap of two (6,3) nets, but in fact it only contains congruent quadrangles similar to those of the (4,4) net.10 Although CdI2-type networks are usually reported in inorganic compounds, only a few examples were found in the metal–organic coordination frameworks.11 This anionic layer represents the first non-interpenetrating CdI2-type network in a metal tricarboxylate system.

The 2D layers and the pentanuclear copper clusters are linked by the cyclic (H2O)18 clusters via hydrogen bonds to generate a 3D supramolecular framework (Table S1 in the Supporting Information). The resultant 3D framework possesses 1D channels along the a axis with a channel diameter of 6.7 Å (the channel size is measured by considering van der Waals radii for constituting atoms). The cavities of the framework are occupied by the main parts of centrosymmetric cyclic (H2O)18 clusters, which contain two octamer water rings and six dangling water molecules (Figure 3b). In the (H2O)18 cluster, O5W, O13W, O7W, O12W, O11W, and O9W are hydrogen-bonded to their equivalents derived by a crystallographic inversion center to form a (H2O)18 subunit, which contains two equivalent distorted octamer water rings sharing four edges. Although a variety of discrete water clusters, involving hexamers, octamers, decamers, dodecamers, hexadecamers, and even a magic number (H2O)21 cluster, have been structurally characterized,12 so far such a discrete (H2O)18 cluster consisting of two distorted octamer

of view, a 1:1 mixture of \([\text{Cu}_5(\text{tci})_2(\text{OH})_2(\text{H}_2\text{O})_8]^{2-}\) represents 25.7% per unit cell volume.

The thermal stability of 1 was examined by thermogravimetric analysis (TGA) in a dry nitrogen atmosphere from 35 to 900 °C. The first weight loss of 8.98% from 50 to 155 °C corresponds to the loss of all lattice water molecules (calcd 9.04%), which then began to decompose upon further heating (Figure S1 in the Supporting Information).

The temperature-dependent magnetic susceptibilities of 1 were collected on polycrystalline samples with random orientation (Figure 4). At 300 K, the \(\chi_mT\) product (2.670 \(\text{cm}^3 \text{mol}^{-1} \text{K}^{-1}\)) is very close to the spin-only value (2.625 \(\text{cm}^3 \text{mol}^{-1} \text{K}^{-1}\)) for seven magnetically isolated Cu\(^{II}\) ions. Starting from room temperature, the \(\chi_m\) values decrease gradually to 0.99 \(\text{cm}^3 \text{mol}^{-1} \text{K}^{-1}\) at 2.0 K. The data between 300 and 100 K were fitted by the Curie–Weiss law with \(C = 3.22(1) \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}\) and \(\theta = -64(1) \text{ K}\) (Figure S3 in the Supporting Information). The negative Weiss constant indicates that strong antiferromagnetic coupling dominates this system. Because compound 1 is, from a structural point of view, a 1:1 mixture of \([\text{Cu}_5(\text{tci})_2(\text{OH})_2(\text{H}_2\text{O})_8]^{2-}\) and \([\text{Cu}_2(\text{tci})_3]^{2+}\) building units, it is straightforward to postulate that the magnetic properties of 1 must be the sum of those from above all because both building units also appear isolated in compound 1. Accordingly, we have fitted the magnetic data of 1 with a Hamiltonian operator: \(H_{\text{ex}} = -2J_1S_1S_2 - 2J_2S_3(S_4 + S_5 + S_6 + S_7) - 2J_3(S_4S_5 + S_6S_7)\), where \(J_1\) is the intradimer exchange interaction through four carboxylate bridges and \(J_2\) and \(J_3\) are the intrapentamer coupling exchange interaction through mixed \(\mu_3\)-hydroxyl, syn,syn, and 1,1,3-\(\mu_3\)-carboxylate bridges within \(\text{Cu}_5\) units. When we have assumed that all of the Cu\(^{II}\) ions in both building units have the same \(g\) factor, the magnetic interactions between long-distant metal pairs in the pentamer are excluded. This model provides very satisfactorily the experimental data in the range of 10–300 K with the following parameters:

\[
\begin{align*}
J_1 &= -3.3(1) \text{ cm}^{-1} \\
J_2 &= -1.0(1) \text{ cm}^{-1} \\
J_3 &= 0.17(2) \text{ cm}^{-1} \\
T_{\text{IP}} &= 760(4) \times 10^{-6} \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1} \\
R &= 3.3 \times 10^{-4} (\text{TIP is the temperature-independent paramagnetic susceptibility for seven Cu}^{II}\text{ ions, and } R = \sum (\chi_{\text{obs}}T - \chi_{\text{calc}}T)^2 / \chi_{\text{calc}}^2).\end{align*}
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The coupling values suggest that the antiferromagnetic interaction between the Cu ions from \(\text{Cu}_2\) units through four syn,syn carboxylate bridges is obviously larger than the antiferromagnetic coupling between the neighboring Cu\(^{II}\) from \(\text{Cu}_5\) units.

As expected, the \(J_1\) value is comparable to those of the reported 2D Cu\(^{II}\) framework with similar dimeric Cu\(_5\)(nic)\(_4\)-based bridges (nic = nicotinate; \(J = -160 \text{ cm}^{-1}\))\(^{(15)}\) and Cu\(_5\)(5-nbdcc)\(_2\)-based bridges (5-nbdcc = 5-nitro-1,3-benzenedicarboxylate; \(J = -158 \text{ cm}^{-1}\)).\(^{(16)}\) On the other hand, a search in the CCDC database shows five similar Cu\(^{II}\) pentamers with a central Cu\(^{II}\) center connected to four adjacent Cu\(^{II}\) centers only via \(\mu_3\)-OH groups and syn,syn carboxylate bridges.\(^{(17)}\) Unfortunately, only one of five Cu\(^{II}\) pentamers reported to date has been magnetically characterized and presents antiferromagnetic and ferromagnetic coupling (\(g = 2.22, J = -11 \text{ K}, \text{ and } J' = 62.5 \text{ K}\)).\(^{(15)}\) Such magnetic properties for Cu\(_5\) units may arise from a cooperative magnetic effect of mixed \(\mu_3\)-hydroxyl, syn,syn, and 1,1,3-\(\mu_3\)-carboxylate bridges.

In summary, a novel 3D supramolecular framework that contains 2D noninterpenetrating CdI\(_2\)-type networks, pentanuclear Cu\(^{II}\) clusters, and cyclic (H\(_2\)O)\(_8\) clusters has been assembled from the tci ligand and the Cu\(^{II}\) ion. The combination of the cis,cis,cis conformation of the ligands leads to the pentanuclear Cu\(^{II}\) clusters, while the resultant CdI\(_2\)-type layer may be attributed to the cis,trans,trans conformation of the tci ligands. The successful synthesis of 1 not only provides a perfect molecular recognition and a mutual host–guest stability of the coordination framework but also proves that the flexible organic ligand with highly flexible arms may generate novel structures.

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Supporting Information Available: Experimental procedures, structure figures, TGA, simulated and experimental powder X-ray diffraction patterns, magnetic data and crystallographic data (CIF), and hydrogen bonds for the compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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