

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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Received November 15, 2009

The anionic CdI₂-type topological net, [Cu₂(tci)₂]²⁻, and the pentanuclear copper cluster cation [Cu₅(tci)₂(OH)₂(H₂O)₈]²⁺ [tci = tris(2-carboxyethyl)isocyanurate] form a complementary 3D supramolecular framework. Interestingly, there exist centrosymmetric cyclic (H₂O)₁₈ 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 progress is highly influenced by several factors,³ such as the metal/ligand nature, solvent, templates, and counterions. As good candidates for rigid tripodal spacers 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 (H₃tci), 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 H₃tci ligand, namely, [Cu₅(tci)₂(OH)₂(H₂O)₈][Cu₂(tci)₂] · 11H₂O (**1**). This compound is interesting for several reasons: (i) the anionic portion of the structure forms a noninterpenetrated CdI₂-type layer not observed with Cu²⁺ and simple anions; (ii) the formation of the CdI₂-type anionic layer is enabled by charge compensation via a complex cation, rare for a coordination solid;⁶ (iii) the compound's countercation itself is a pentanuclear copper(II) cluster, which is stabilized by incorporation as part of the ion pair; (iv) in the cavities of this host–guest compound, there exist rare cyclic (H₂O)₁₈ clusters. This is an unusual example of molecular recognition and a mutual structural stabilization effect in a coordination framework.

Compound **1** was synthesized from a mixture of H₃tci and copper acetate at room temperature (see the Supporting Information). Single-crystal X-ray analysis⁷ reveals that **1** is a 2D anionic layer and a pentanuclear cationic cluster concomitant compound. Although a relevant example consisting of 2D anionic “star” nets and trinuclear Fe^{III} cations was reported recently,⁸ such cases are still rare. To the best of our knowledge, this is the first example containing a pentanuclear cation and a 2D anion layer. The asymmetric unit contains three and a half Cu^{II} centers, two tci ligands,

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(7) Crystal data for **1**: triclinic; space group *P* $\bar{1}$ (No. 2); *a* = 11.861(1) Å; *b* = 12.855(2) Å; *c* = 16.875(2) Å; α = 71.216(2)°; β = 79.836(2)°; γ = 65.431(1)°; *V* = 2212.6(4) Å³; *Z* = 1; *D*_c = 1.644 g cm⁻³; *F*(000) = 1119; μ = 1.761 mm⁻¹; 12 113 reflections measured; 8515 unique (*R*_{int} = 0.0243); final *R*1 = 0.0640; *wR*2 = 0.1910; *S* = 1.023 for all data. CCDC number: 725481.

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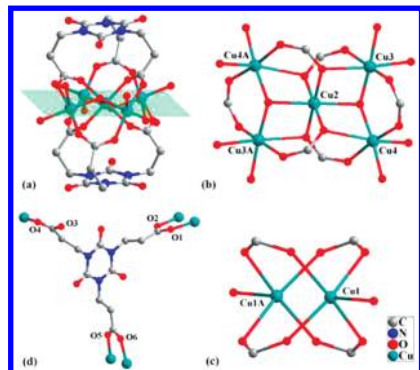


Figure 1. Coordination modes of tci ligands in a pentanuclear copper cluster (a) and in a 2D layer (d). Coordination environment of Cu^{II} centers in a pentanuclear copper cluster (b) and in a 2D layer (c) showing a paddlewheel cluster in **1**.

one μ_3 -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 Cu^{II} 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 μ_3 -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 aqua ligands, one μ_3 -OH group, and two carboxylate oxygen atoms of two distinct tci ligands. The octahedrally coordinated Cu2 is connected to four adjacent copper centers via two μ_3 -OH groups (Figure 1b), in which the five copper centers are all coplanar and arranged in two symmetric Δ -type patterns ($\text{Cu}2 \cdots \text{Cu}3$ 3.102 Å; $\text{Cu}2 \cdots \text{Cu}4$ 3.256 Å; $\text{Cu}3 \cdots \text{Cu}4$ 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 Cu^{II} 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 Cu^{II} 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 conformation. The energy barrier between the cis,cis,cis and cis,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 **1** is that the 2D layer can be rationalized as a noninterpenetrating CdI_2 -type network by simplifying the tci ligand as a 3-connecting node (vertex symbol 4^3) and the $\text{Cu}^{\text{II}}-\text{Cu}^{\text{II}}$ dimer as a 6-connecting node (vertex symbol $4^6 6^6 8^3$) (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 CdI_2 -type network, which can be represented by Wells notation $\{4_6^3\}$, is one of the Catalan nets

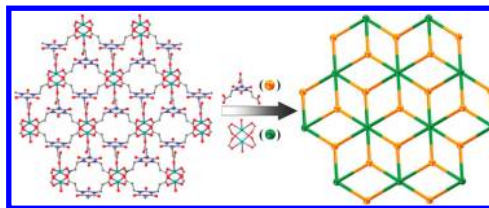


Figure 2. Perspective view of a 2D layer in **1** (left) and schematic view of the layer showing CdI_2 -type topology (right).

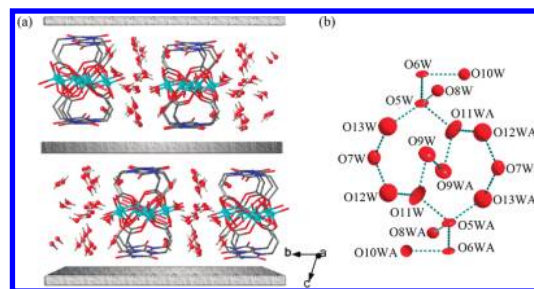


Figure 3. (a) Schematic view of the 3D framework of **1** showing the 2D CdI_2 layers, pentanuclear copper clusters, and $(\text{H}_2\text{O})_{18}$ clusters. (b) Centrosymmetric cyclic $(\text{H}_2\text{O})_{18}$ cluster observed in **1**.

known in inorganic compounds such as metal alkoxides and hydroxides.⁹ The main topological character of the CdI_2 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 CdI_2 -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 CdI_2 -type network in a metal tricarboxylate system.

The 2D layers and the pentanuclear copper clusters are linked by the cyclic $(\text{H}_2\text{O})_{18}$ 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 $(\text{H}_2\text{O})_{18}$ clusters, which contain two octamer water rings and six dangling water molecules (Figure 3b). In the $(\text{H}_2\text{O})_{18}$ cluster, O5W, O13W, O7W, O12W, O11W, and O9W are hydrogen-bonded to their equivalents derived by a crystallographic inversion center to form a $(\text{H}_2\text{O})_{18}$ 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 $(\text{H}_2\text{O})_{21}$ cluster, have been structurally characterized,¹² so far such a discrete $(\text{H}_2\text{O})_{18}$ cluster consisting of two distorted octamer

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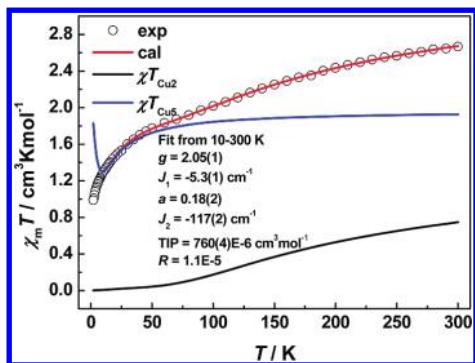


Figure 4. Temperature-dependent magnetic susceptibility of **1** (point, experimental data; red line, simulated curve with the best least-squares fitting; blue line: simulated curve of the Cu₂ layer; black line, simulated curve of the Cu₅ cluster).

water rings in this paper has never been reported. After omitting these lattice water molecules from the channels, PLATON¹³ analysis revealed a void volume of 569.2 Å³ that 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 $\chi_m T$ product (2.670 cm³ mol⁻¹ K⁻¹) is very close to the spin-only value (2.625 cm³ mol⁻¹ K⁻¹) for seven magnetically isolated Cu^{II} ions.¹⁴ Starting from room temperature, the $\chi_m T$ values decrease gradually to 0.99 cm³ mol⁻¹ K⁻¹ at 2.0 K. The data between 300 and 100 K were fitted by the Curie–Weiss law with $C = 3.22(1)$ cm³ mol⁻¹ K⁻¹ and $\theta = -64(1)$ 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 [Cu₅(tci)₂(OH)₂(H₂O)₈]²⁺ and [Cu₂(tci)₂]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: $H_{\text{ex}} = -2J_1 S_1 S_2 - 2J_2 S_3 (S_4 + S_5 + S_6 + S_7) - 2J_3 (S_4 S_5 + S_6 S_7)$, 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 μ_3 -hydroxyl, syn,syn, and 1,1,3- μ_3 -carboxylate bridges within Cu₅

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: $g = 2.05(1)$, $J_1 = -117(2)$ cm⁻¹, $J_2 = -5.3(1)$ cm⁻¹, $J_3 = -1.0(1)$ cm⁻¹, TIP = 760(4) × 10⁻⁶ cm³ mol⁻¹, and $R = 3.3 \times 10^{-6}$ (TIP is the temperature-independent paramagnetic susceptibility for seven Cu^{II} ions, and $R = [\sum(\chi_{\text{obs}} T - \chi_{\text{calc}} T)^2 / \sum(\chi_{\text{obs}} T)^2]$). The coupling values suggest that the antiferromagnetic interaction between the Cu ions from Cu₂ units through four syn,syn carboxylate bridges is obviously larger than the antiferromagnetic coupling between the neighboring Cu^{II} from Cu₅ units.

As expected, the J_1 value is comparable to those of the reported 2D Cu^{II} framework with similar dimeric Cu₂(nic)₄-based bridges (nic = nicotinate; $J = -160$ cm⁻¹)¹⁵ and Cu₂(5-nbdc)₂-based bridges (5-nbdc = 5-nitro-1,3-benzene-dicarboxylate; $J = -158$ 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 μ_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 ($g = 2.22$, $J = -11$ K, and $J' = 62.5$ K).¹⁵ Such magnetic properties for Cu₅ units may arise from a cooperative magnetic effect of mixed μ_3 -hydroxyl, syn,syn, and 1,1,3- μ_3 -carboxylate bridges.

In summary, a novel 3D supramolecular framework that contains 2D noninterpenetrating CdI₂-type networks, pentanuclear Cu^{II} clusters, and cyclic (H₂O)₁₈ 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 CdI₂-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.

Acknowledgment. This work was granted financial support from the National Natural Science Foundation of China (Grantd 20871063 and 20871034) and the Program for New Century Excellent Talents in University of the Ministry of Education China (Grant NCET-07-217).

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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