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Catenation of Loop-Containing 2D Layers with a 3D pcu Skeleton into a New Type of Entangled Framework Having Polyrotaxane and Polycatenane Character

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Catenation of 2D layers of rings with a 3D frame of pcu topology gives a new type of entangled framework incorporating functional, nanosized polyoxoanions, which exhibits both polycatenane and polyrotaxane character.

Entangled systems have captivated much attention of chemists not only for their undisputed beauty[1–3] but also for their potential applications arising directly from the intertwining nature of the lattices.[4] Many topologically interesting entangled structures have been discussed in comprehensive reviews by Batten and Robson[5] and Ciani and co-workers.[6] Among these, one particularly intriguing phenomenon is mutual interlock involving motifs of different dimensionalitites. Although a variety of hypothetical species belonging to this theme could be envisaged as enumerated by Ciani et al.,[6a] the known examples are true rarities: these include four (1D + 2D) polycatenated species[7] and five intermediate cases between interpenetration and polycatenation, exhibiting inextricable (1D + 3D) and (2D + 3D) arrays.[8] Surprisingly, the structural motifs in all of these species are exclusively confined to 1D ribbons of rings, 2D planar square grid layers, and 3D frames of $\mathrm{CdSO_4}$ (cds) topology. An interesting question that arises from this is whether entangled structures of this family can also be generated by other types of motifs, and, if so, what would they be like?

Fortunately, during further investigations into entangled systems,[9] we have isolated such a complex, namely, $[\mathrm{Cu^I_3(L)_3}][\{\mathrm{Cu^{II}(L)_2}\}\{\mathrm{PMo_{12}O_{40}(VO)_2}\}]\cdot\mathrm{H_2O}$ (**1**) (L = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene), in which loop-containing 2D layers are catenated to a 3D frame of pcu ($4^{12}6^3$, α-Po) topology (see Chart 1). The entanglement found here, of the (2D + 3D) type, is of particular interest from the topological point of view in the following ways: (i) prior to this work, the cds net was the sole type of 3D net used to construct (1D + 3D) and (2D + 3D) arrays. This is not surprising taking into account the fact that it is a self-dual net and has large voids that can be occupied by one or more

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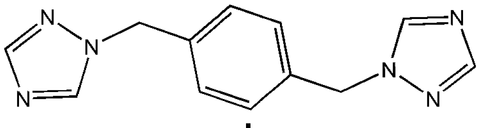
Chart 1



L

independent motifs.[10] In principle, other self-dual nets, such as dia, pcu, and srs, could also be capable of giving the aforementioned arrays in their own right; however, no actual example has been as yet characterized. Thus, compound **1** provides a real model for this hypothesis; again, a theoretically possible but never observed mode is accomplished in the area of coordination polymers. (ii) The 2D sheet of rings in **1**, rather than the planar (4,4) grids occurring in this type of entanglement, makes it a rare case having both polyrotaxane and polycatenane character.[11] (iii) Polyoxometalates, as anionic early transition-metal oxide clusters, have many properties that make them attractive for applications in catalysis, biology, magnetism, optics, and medicine.[12] One of the most important properties of these O-enriched anionic clusters is their ability to undergo reversible multielectron redox processes when responding to electro- or photochemical stimuli. It has been highly expected by Yaghi[13] that metal−organic frameworks are constructed from well-defined units that are in themselves capable of responding to a stimulus. As an extension of our previous work where nanosized Keggin anions are encapsulated in a 3D polyrotaxane framework as guests,[9d] compound **1** represents the first example of incorporating functional polyoxoanions into this new type of entanglement and, therefore, in the longer term, opens opportunities for investigating the nature of polyoxoanions within such a system.

The reaction of L with $Cu(NO_3)_2 \cdot 3H_2O$, $H_3PMo_{12}O_{40}$, and NH_4VO_3 under hydrothermal conditions resulted in black crystals of **1** (see Supporting Information). The product is stable in the air, and the framework only begins to decompose when heated to 275 °C (Figure S1, Supporting Information).

Single-crystal X-ray analysis[14] reveals that **1** consists of two distinct and cyrstallographically independent polymeric motifs in the crystal. One motif is a loop-containing sheet (Figure 1a,b), in which two crystallographically independent Cu^I atoms display linear (Cu−N 1.855(11) Å, N−Cu−N 180.0(2)°) and trigonal-planar (Cu−N 1.829(14)−2.020(11) Å) coordination geometry, respectively (Figure S2a, Supporting Information). Two types of L ligands exist in the sheet: one assumes a "U"-type conformation (L^u) bridging two three-coordinated copper centers into a 26-membered $Cu_2(L)_2$ ring, the other adopts a "Z"-type conformation (L^z) bridging four copper atoms in an exotetradentate coordination mode (Figure S3, Supporting Information). Significantly, a search in the Cambridge Structural Database reveals that, up to now, only the μ_2-coordination mode has been established for L; this is the first observation of the "tetradentate μ_4-bridging" mode. As a result of this new bridging fashion, the 2D sheet of rings, of composition $[Cu^I_3(L)_3]$, can therefore be described as being formed by $Cu_2(L^u)_2$ loops interlinked by Cu−L^z polymeric chains. An interesting structural feature of the 2D sheet consists of the simultaneous presence of a tetragonal mesh (15.4 × 14.6 Å) and a 26-membered loop (9.1 × 9.9 Å). It is, moreover, noteworthy that the two types of windows are oriented at an angle of ca. 82°, and this constitutes a potential factor for generating rotaxane-like links considering two previously reported cases of (2D → 2D) polythreading based on two such layers.[11a,b]

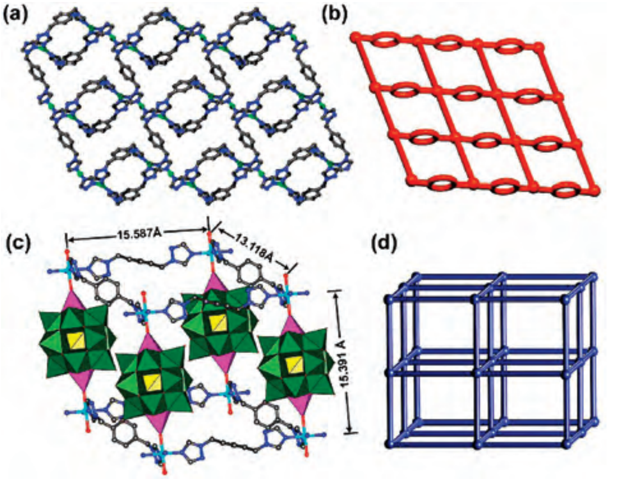


Figure 1. Two different motifs in **1**: perspective (a) and schematic views (b) of the 2D loop-containing layer and a single distorted cubelike unit (c) of the 3D **pcu** net (d).

The other polymeric motif is a single three-dimensional network built from bivanadyl-capped, highly reduced Keggin polyanions $[PMo^V_6Mo^{VI}_6O_{40}(V^{IV}O)_2]^{5-}$, Cu^{II} ions, and L ligands (Figure S4, Supporting Information). The polyoxoanion can be best described as a bicapped Keggin structure that is essentially built on an α-Keggin core $\{PMo_{12}O_{40}\}$ capped by two {VO} units.[15] The Cu^{II} center is connected to four adjacent ones at distances of 13.118 and 15.587 Å through four L^z ligands to form 2D layers of composition $[Cu^{II}(L)_2]$. These sheets are further cross-linked by bicapped Keggin polyoxoanions in virtue of terminal oxygen atoms bound to Cu centers to generate a single 3D network with pcu topology that possesses distorted cubelike units of

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(14) Crystal data for **1**: M_r = 3429.69, triclinic, space group $P\bar{1}$, a = 13.118(3) Å, b = 14.624(3) Å, c = 15.193(3) Å, α = 95.00(3)°, β = 114.61(3)°, γ = 111.88(3)°, V = 2355.2(8) Å^3, Z = 1, ρ_{calcd} = 2.418 mg m^{-3}, final R_1 = 0.0686 for 8054 independent reflections [$I > 2\sigma(I)$]. CCDC 626881. One triazole ring coordinated to the Cu2 atom is disordered (N4 N5 N6 C7 C10) and modeled using two sets of positions with site occupancies which refined to 60% and 40% (see Supporting Information).

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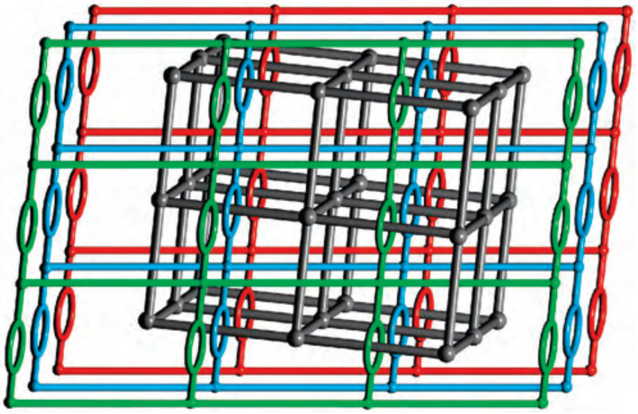

Figure 2. A schematic presentation of the overall (2D + 3D) entangled network.

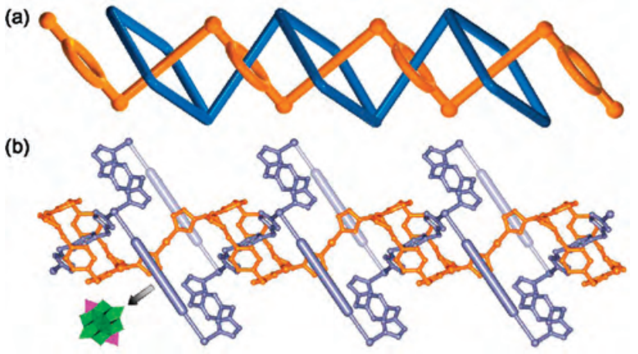

Figure 3. Schematic (a) and perspective (b) representations of the polyrotaxane columns in **1**. Orange parts come from the 2D sheet of loops, and blue parts come from the 3D **pcu** network.

dimensions 15.587 × 13.118 × 15.391 Å (Figure 1c,d and Figure S5, Supporting Information). The coordination geometry of Cu^{II} centers, different from those observed in the first motif, is octahedral with two axial-bonded oxygen atoms (Cu−O 2.020(7) Å) from two polyoxoanions and four equatorial nitrogen atoms (Cu−N 2.096(10) Å) from four L ligands (Figure S2, Supporting Information).

The most outstanding structural feature of **1** is that the loop-containing 2D layers are inextricably entangled with the 3D frame in an intricate, unprecedented manner. As illustrated in Figure 2, the layers stack parallel along the [0 0 1] direction, with a separation of 11.4 Å and a lateral offset of 1/4 the tetragonal mesh width; all of the "loops" and "square meshes" of the sheets are involved in catenation with the smallest rings of the 3D pcu net, and each cubelike unit of the 3D net has components of two independent sheets passing through it. As a result, the loops of the 2D layer are threaded by the longest rods (node-to-node distance of 15.587 Å) of the 3D net (this can be appreciated considering the steric hindrance), and in turn, the rods of the 2D layer pass through the given rectangular windows (dimensions 13.118 × 15.391 Å) of the 3D net. Thus, the resultant entangled framework could equally well be considered formed by interconnected parallel 1D polyrotaxane columns (Figure 3 and Figure S6, Supporting Information). To date, only four examples showing the polyrotaxane/polycatenane associations, to the best of our knowledge, have been characterized, all constructed from the same motifs.[11] Therefore, compound **1** represents the first exceptional case assembled from polymeric motifs of different dimensionality.

The incorporation of a functional polyoxoanion, as expected, endows this species with electrochemical activity and electrocatalytic properties. The cyclic voltammetric behavior for a **1**-modified carbon paste electrode (**1**-CPE) in 1 M H_2SO_4 aqueous solution at different scan rates was recorded, showing three well-defined redox couples (I−I′, II−II′, and III−III′) in the potential range of +800 to −100 mV, attributable to the $[PMo_{12}O_{40}(VO)_2]^{5-}$ polyoxoanion (Figure S7, Supporting Information).[11b,16] At scan rates lower than 150 mV/s, the peak currents were proportional to the scan rate, suggesting that the redox process is surface-controlled; however, at scan rates higher than 150 mV/s, the peak currents were proportional to the square root of the scan rate, which indicates that the redox process is diffusion-controlled (Figure S8, Supporting Information).[17] **1**-CPE displays electrocatalytic activity toward the reduction of nitrite (Figure S9, Supporting Information). On the addition of modest amounts of NO_2^-, the reduction peak currents increase and the corresponding oxidation peak currents decrease dramatically, indicating that the three reduced species all have electrocatalytic activity for nitrite reduction. It was also noted that the third reduced species showed the best electrocatalytic activity; that is, the catalytic activity is enhanced with an increasing extent of polyoxoanion reduction. The voltammetric behavior of **1**-CPE almost stays unchanged over 500 cycles, and when **1**-CPE was stored at room temperature for 2 months, the current response remained almost unchanged, which proved that it was very stable. Moreover, the electrode surfaces could be renewed by squeezing a little carbon paste out of the tube. This is especially useful for electrocatalytic studies since the catalytic activity is known to decrease when the electrode is fouled.

In conclusion, a new type of entanglement involving 2D layers of rings catenated to a 3D pcu network has been presented, highlighting an intriguing feature of coordinative network chemistry in producing rich architectures and topologies. This work, besides representing an intriguing example of chemical topology, may open new perspectives for generating functional entangled frameworks considering the incorporation of polyoxoanions.

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Supporting Information Available: Details of the syntheses, IR, TG, XRPD, and complementary drawings for crystal structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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