Inorg. Chem. **2007**, *46*, 4365–4367

Inorganic Chemistry
Communication

A Rare Chiral Self-Catenated Network Formed by Two Cationic and One Anionic Frameworks

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Received February 8, 2007

A chiral heterometallic complex, obtained from the solvothermal reaction of [Zn(4-pytpy)$_2$](BF$_4$)$_2$ [4-pytpy = 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine] and CuCN, exhibits a rare self-catenated network formed by two 3D cationic and one 3D anionic frameworks.

Entangled systems have been achieving rapidly increasing attention not only for their complicated and even aesthetic architectures and topologies[1] but also for their potential application in functional materials.[2] It is well-known that catenanes, rotaxanes, and molecular knots occupy important places in the area of molecular entanglement.[3] Interpenetrating network structures, regarded as "infinite, ordered polycatenanes or polyrotaxanes",[3a] are characterized by the presence of two or more independent frameworks that are inextricably entangled through the rings belonging to one framework. If *n*-fold interpenetrating networks are connected by bridging ligands or hydrogen bonding/weak interactions, another intriguing type of entanglement, self-penetration, can be achieved. Thus, self-penetration is a single network having the peculiarity that the smallest topological rings are catenated by other shorter rings belonging to the same net. Although many self-catenated nets exhibiting various topologies and/or chemical compositions have been reported, few examples of self-catenated structures containing both 3D cationic and anionic coordination polymer aggregates were reported up to now, especially those exhibiting chiral properties. Therefore, the strategy to construct self-catenated networks composed of cationic and anion frameworks is still a puzzle to be revealed.

Moreover, heterometallic coordination complexes prepared by step synthesis have drawn increasing attention. Polydentate ligands are chosen in the first step synthesis of metalloligands because they chelated metal ions firmly, and then the free coordination sides can combine other metal ions to form the resulting complexes. This approach is extremely modular because the use of different metal ions and ligands will afford metalloligands with different geometries and spectroscopic characteristics, giving rise to heterometallic complexes with a variety of structures and physical properties, such as their porous,[4] incorporating magnetic,[5] and fluorescence properties.[6]

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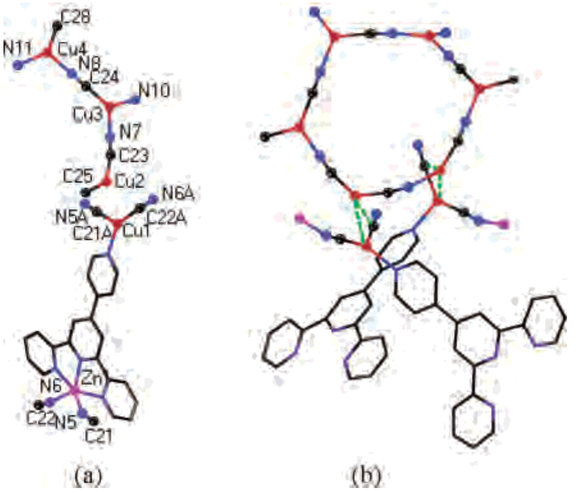

Figure 1. (a) Coordination environments of Cu and Zn atoms in **1**. (b) **1**: one anionic component $[Cu_6(CN)_8]^{2-}$ (upper) and two cationic components $[ZnCu(CN)_2(4\text{-pytpy})]^+$ (lower) linked by Cu···Cu and Cu···C interactions (green dotted lines).

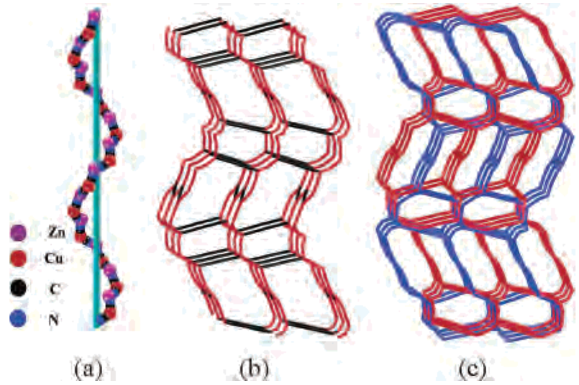

Figure 2. (a) Single right-handed $[ZnCu(CN)_2]^+$ helix in the cationic framework $[ZnCu(CN)_2(4\text{-pytpy})]^+$. (b) 3D cationic framework constructed of $[ZnCu(CN)_2]^+$ helices (red) and 4-pytpy linkers (black). (c) 2-fold interpenetration (red and blue) of 3D cationic frameworks.

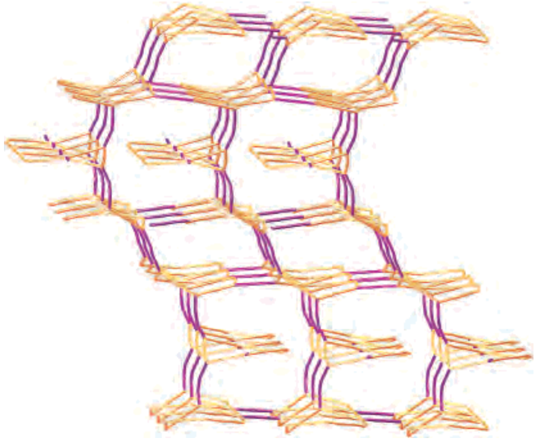

Figure 3. 3D anionic framework $[Cu_6(CN)_8]^{2-}$ constructed of six-CuCN rings (golden) and CN^- linkers (purple).

Herein, a new $d^{10}-d^{10}$ heterometallic complex $[ZnCu(CN)_2(4\text{-pytpy})]_2[Cu_6(CN)_8]$ [**1**; 4-pytpy = 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine] was obtained by a solvothermal reaction of copper(I) cyanide with presynthesized $[Zn(4\text{-pytpy})_2](BF_4)_2$ in a molar ratio of 8:1 at 140 °C.[7] In the starting reactant $[Zn(4\text{-pytpy})_2](BF_4)_2$, as a metalloligand, each terpyridine ligand chelates a Zn^{II} ion using tridentate pyridyl sites to form a monomer, leaving the pendent monodentate pyridyl site for further coordination. The product is very stable in air and began to decompose when heated to as high as 320 °C (Figure S1 in the Supporting Information).

Single-crystal X-ray diffraction[8] shows that the asymmetric unit of **1** contains four Cu and one Zn crystallographically nonequivalent atoms (Figure 1a). The four monovalent Cu atoms all exhibit three-coordination geometries. The Cu1 atom is coordinated by the N atom from the pendent monodentate pyridyl of 4-pytpy and CN^- anions to give a trigonal geometry. The Cu2 atom is coordinated by CN^- anions in an angular geometry [C25−Cu2−C23 135.1°]. The Cu3 and Cu4 atoms are both coordinated by CN^- anions to complete the trigonal environment. Meanwhile, Zn1 in an almost square-pyramidal geometry is bound by two CN^- anions and three N atoms from 4-pytpy.[9] This is due to the facts that one 4-pytpy was broken off from $[Zn(4\text{-pytpy})_2](BF_4)_2$ and the Zn^{II} vacant sites were approached by CN^- anions during the synthesis.

As a whole, complex **1** consists of three separated components: two cationic frameworks $[ZnCu(CN)_2(4\text{-pytpy})]^+$ and one anionic framework $[Cu_6(CN)_8]^{2-}$ (Figure 1b). The cationic framework contains a 1D right-handed mixed-metal (Zn and Cu) cyanide helix $[ZnCu(CN)_2]^+$ (Figure 2a) and is then linked by 4-pytpy to extend to a 3D framework (Figure 2b). The framework can be abstracted into a uninodal bto network [or the vertex symbol of $(10)(10^2)(10^2)$] by denoting the Cu and Zn atoms as 3-connected nodes and CN^- anions and 4-pytpy as spacers (Figure S2 in the Supporting Information). Two identical cationic 3D frameworks interpenetrated, mutually incorporating a 2-fold interpenetration structure (Figure 2c). In the anionic framework $[Cu_6(CN)_8]^{2-}$, six Cu atoms and six CN^- anions form a six-CuCN ring (upper component in Figure 1b). The rings (golden in Figure 3) are linked by CN^- anions (purple in Figure 3) to extend to a 3D network, a binodal network of

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[7] Synthesis of **1**: A mixture of CuCN (0.036g, 0.4mmol) and $[Zn(4\text{-pytpy})_2](BF_4)_2$ (0.043g, 0.05mmol) in a mole ratio of 8:1 in acetonitrile (6 cm^3) was sealed in a 15 cm^3 Teflon-lined reactor and heated to 140 °C for 72 h and then cooled to room temperature at a rate of 6 °C/h. X-ray-quality black crystals of compound **1** were obtained in ca. 14% yield. Anal. Calcd for $C_{26}H_{14}Cu_4N_{10}Zn$: C, 39.73; H, 1.80; N, 17.82. Found: C, 39.85; H, 1.75; N, 17.81. IR (KBr, cm^{-1}): 2116s, 1602m, 1569w, 1544m, 1473m, 1408m, 1242w, 1156w, 1070w, 1017w, 792m, 653w, 506w, 461w.

[8] Crystal data for complex **1** (CCDC 643800): hexagonal, space group $P6(1)22$, $M = 786.00$, $a = 14.6465(6)$ Å, $b = 14.6465(6)$ Å, $c = 41.974(3)$ Å, $V = 7797.9(8)$ Å^3, $Z = 12$, $\rho_{calcd} = 2.009$ g/cm^3, $\mu = 4.168$ mm^{-1}, $F(000) = 4632$, $T = 298(2)$ K; R1 = 0.0539, wR2 = 0.1018, GOF = 1.122, for all data. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo Kα, $\lambda = 0.70173$ Å) using *SMART* software. Reflection intensities were integrated using *SAINT* software, and absorption correction was applied semiempirically. The structures were solved by a direct method and refined by full-matrix least squares against F^2. Anisotropic thermal parameters were applied to all non-H atoms. The H atoms were generated geometrically (C−H = 0.930 Å). The crystallographic calculations were conducted using the *SHELXL-97* programs. The assignment of the absolute structures for **1** was confirmed by the refinement of the Flack enantiopole parameter to values of 0.0392.

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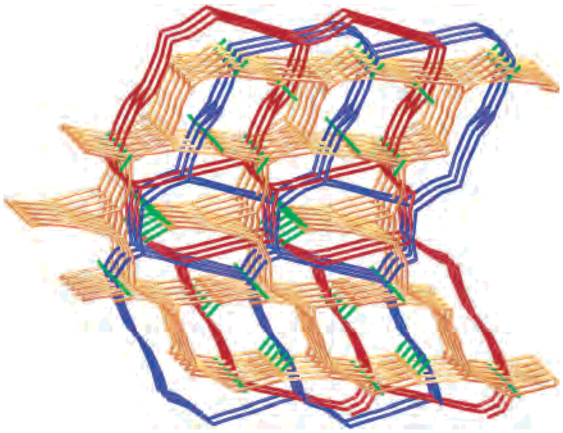

Figure 4. 3-fold interpenetration structure derived from two cationic frameworks (red and blue) and one anionic framework (golden) connected by Cu···Cu and Cu···C interactions (green).

$(4,16^2)(4,16^2)$, by treatment of the Cu3 and Cu4 atoms as 3-connected nodes and CN^- anions and Cu−C/N as spacers (Figure S3 in the Supporting Information).

Interestingly, **1** can be described as a 3-fold hetero-interpenetrating structure with two 3D cationic $[ZnCu(4\text{-}pytpy)(CN)_2]^+$ and one anionic $[Cu_6(CN)_8]^{2+}$ frameworks[10] (Figure 4). In this structure, interactions exist between Cu atoms and the adjacent N and Cu atoms. The Cu···C/N and Cu···Cu distances of 2.547(1) and 2.639(1) Å, respectively, are below the sum of their van der Waals radii, 2.95 and 2.80 Å, respectively. Taking the interactions into account, the structure clearly exhibits a self-catenated network because it is generated from the cross-linking of two 3D cationic and one 3D anionic frameworks through Cu···Cu and Cu···C interactions. When Cu1 is denoted as a 4-connected node and other metal atoms are denoted as 3-connected nodes, the framework can be abstracted into a 5-nodal net of $(10^3)(10^6)(6,10,12)(6,10^2)_2$. The schematic representation of the network also reveals that it is a self-catenated network, and some of the shortest circuits of the network are penetrated by links in the same network. As highlighted in Figure S4 in the Supporting Information, there are 10-membered shortest circuits that are penetrated by one rod.

Because the infinite $[ZnCu(CN)_2]^+$ chains in the cationic framework gave rise to helices with the same right-handness, we referred to the net as a whole in this case as being "right-handed". However, the chirality of the crystals of the complex was further confirmed by solid-state circular dichroism (CD) spectroscopy (Figure S5 in the Supporting Information), which showed no evident signal in this complex, suggesting that the preference for a particular chirality was roughly 1:1. As a result, the complex is a racemate.

Examples of self-interpenetrating frameworks cross-linked by weak interactions are really few.[11] Most reported self-catenated coordination polymers are constructed of neutral networks. The only interpenetrating network containing both cationic and anionic components is a 4-fold structure comprising 2-fold interpenetrating anionic networks and 2-fold interpenetrating cationic ones reported by Zheng et al.[12] Hence, our work represents the first example of a chiral self-catenated structure generated from 3D cationic and anionic frameworks.

In summary, we have prepared a rare chiral self-catenated structure formed through cross-linking of two cationic and one anionic networks connected by ligand-unsupported Cu···Cu and Cu···C interactions. The successful obtainment of this type of network provides a remarkable example of an entangled system.

Acknowledgment. We gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (Grants 20571050 and 20271031) and the Natural Science Foundation of Guangdong Province of China (Grant 021240).

Supporting Information Available: Crystallographic data in CIF format and thermogravimetric analysis and figures showing the topology and solid-state CD spectrum of the complex in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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