

## Two Polyknotted Topological Isomers of Copper(I) 3,5-Bis(4-pyridyl)pyrazolates

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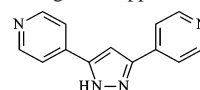
Received June 24, 2006

Two unprecedented 3D polyknotted isomers, arisen from different linkage modes of  $\text{SCN}^-$ , were obtained from 3,5-bis(4-pyridyl)-1*H*-pyrazole (Hbppz) and  $\text{CuSCN}$  under different conditions.

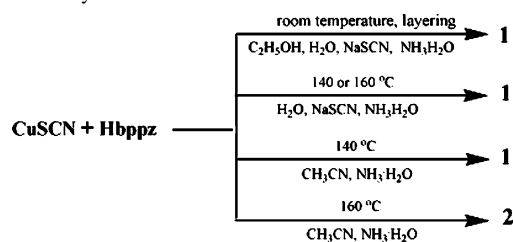
Supramolecular isomerism is an essential element in crystal engineering of coordination polymer frameworks because of not only their structural diversity but also their potential application.<sup>1</sup> Diversity of coordination modes, flexibility in ligands, and subtle environmental changes play some important roles in the formation of isomers.<sup>2–4</sup> Topological isomerism as an important supramolecular isomerism was widely encountered in crystal engineering.<sup>4</sup>

On the other hand, entangled systems as another major theme of supramolecular chemistry are becoming a hot topic owing to their aesthetics and complicated architectures and topologies.<sup>5</sup> Different kinds of entangled supramolecular complexes, including interpenetration, polycatenation, polythreading, polyknotted, and so on, have been reviewed.<sup>5</sup> In

Chart 1. Structure of the Ligand Hbppz



Scheme 1. Synthesis of the Two Isomers



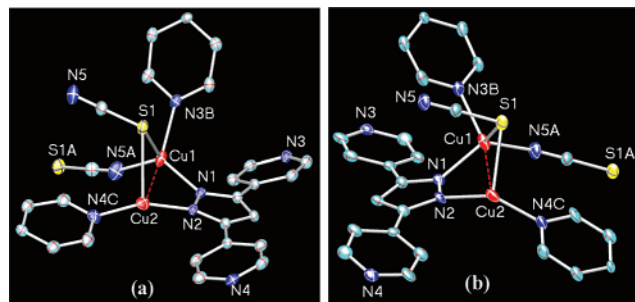
these systems, a small number of coordination compounds exhibit polyknotted network architectures<sup>6</sup> that are built through the cross-linking of different types of interpenetrating networks by bridging connector ligands and by hydrogen-bonding/weak interactions.<sup>5b</sup> Obviously, with different linkage modes, 3D polyknotted networks can be formed, being labeled as polyknotted topological isomers. Unfortunately, polyknotted topological analogues have not been reported to date<sup>1</sup> though an enormous number of isomers are known in classical coordination chemistry.<sup>1–4</sup>

We report herein two 3D polyknotted topological isomers (**1** and **2**) that were obtained from the reactions of copper(I) thiocyanate and 3,5-bis(4-pyridyl)-1*H*-pyrazole (abbreviated as Hbppz, Chart 1) under different conditions (Scheme 1). **1** can be prepared in different solvents and temperatures, whereas **2** was obtained only in acetonitrile and a higher temperature (160 °C), indicating that in acetonitrile a higher temperature favors the formation of **2**. Hbppz was synthesized by a modified literature procedure<sup>7</sup> from 4-acetylpyridine and methyl isonicotinate as primary materials and was

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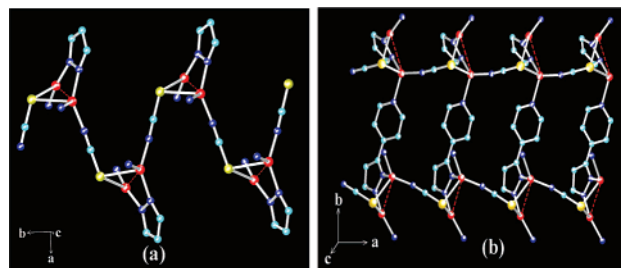
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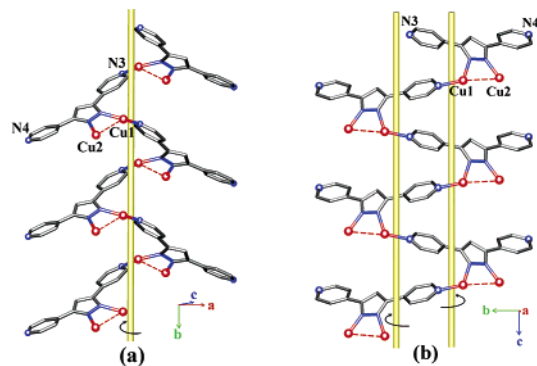
**Figure 1.** Coordination environments of the Cu atoms in **1** (a) and **2** (b). Selected bond distances (Å): **1**, Cu1–N1 1.972(3), Cu1–N3B 2.105(3), Cu1–N5A 1.928(4), Cu1–S1 2.585(1), Cu2–N2 1.903(3), Cu2–N4C 1.915(3), Cu2–S1 2.544(1), Cu1⋯Cu2 3.038(1); **2**, Cu1–N1 2.007(5), Cu1–N3B 2.085(5), Cu1–N5A 1.907(6), Cu1–S1 2.572(2), Cu2–N2 1.917(5), Cu2–N4C 1.922(5), Cu2–S1 2.475(2), Cu1⋯Cu2 2.963(1). Symmetry code: (a) A,  $-x + 1/2, y - 1/2, z$ ; B,  $-x + 1, y + 1/2, -z + 3/2$ ; C,  $x - 1/2, -y + 3/2, -z + 1$ ; (b) A,  $x + 1, y, z$ ; B,  $x, -y + 2, z + 1/2$ ; C,  $x + 1, -y + 1, z + 1/2$ .

characterized by IR, NMR, and X-ray crystallography (Supporting Information).

In isomers **1** and **2**,<sup>8</sup>  $[\text{Cu}_2(\text{bppz})(\text{SCN})]_\infty$ , the deprotonated ligand  $\text{bppz}^-$ , as a tetradentate ligand bearing stronger binding ability than that in its neutral form, binds to four Cu atoms.<sup>9</sup> Of the two symmetry-independent metal atoms of Cu1 and Cu2, Cu1 is four-coordinated in a tetrahedral environment while Cu2 is three-coordinated in a T-shaped geometry (Figure 1). Cu1 and Cu2 atoms are doubly bridged by a pyrazolate from the ligand in an usual exo-bidentate mode of a  $\mu_2$  bridge<sup>9,10</sup> with the four atoms of N1, N2, Cu1, and Cu2 on a slightly distorted plane and a S atom of  $\text{SCN}^-$  adopting a  $\mu_2$ -S bridging mode, resulting in a familiar five-membered (S1–Cu1–N1–N2–Cu2) ring.<sup>9b</sup> On the other hand, each of the Cu atoms is coordinated by one N atom (N3B or N4C) of pyridyl from the second or third  $\text{bppz}^-$  ligand, respectively. Furthermore, only the Cu1 atom is coordinated by the fourth N atom from another  $\text{SCN}^-$ . Therefore, a  $\text{SCN}^-$  anion as a whole acts as a  $\mu_3$  bridge ( $\mu_2$ -S and  $\mu_1$ -N). It is clear that both four-coordinated Cu1 atoms



**Figure 2.** Zigzag and linear chains of  $[\text{Cu}_2(\text{SCN})(\text{pz})]_\infty$  in **1** (a) and **2** (b).



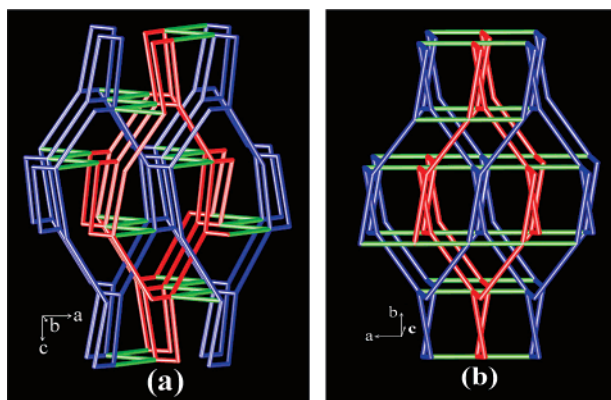
**Figure 3.** 2-fold helical (left-handed) and meso-helical chains of  $[\text{Cu}_2(\text{bppz})]_\infty$  through Cu1 and N3 atoms in **1** (a) and **2** (b).

in the two complexes are chiral. The distances of Cu1 and Cu2 [3.038(1) Å in **1** and 2.963(1) Å in **2**] indicate Cu⋯Cu weak interactions. Compared with those in other 3,5-disubstituted pyrazolate-bridged  $\text{Cu}^I$  complexes,<sup>10</sup> they are obviously shorter.

The main difference in both isomers is the bridging orientation of  $\text{SCN}^-$  (Figure 1). In **1**, the  $\text{SCN}^-$  anion and pyrazolate doubly bridging Cu1 and Cu2 atoms are located on two sides of the triangle plane of Cu1–S1–Cu2. In other words, Cu1 and Cu2 atoms are doubly bridged by  $\text{SCN}^-$  and pyrazolate in a  $\text{trans-}\mu_2$  mode (Figure 1a). However, in **2** they are doubly bridged in a  $\text{cis-}\mu_2$  mode (Figure 1b). Consequently, two quite different chains of  $[\text{Cu}_2(\text{SCN})(\text{pz})]_\infty$  come into being, zigzag chains for **1** along the  $b$  axis on the plane parallel with  $a$  and  $b$  axes, just as if the  $\text{SCN}^-$  anions were reflected back by a set of face-to-face Cu1–S1–Cu2 triangle planes (Figure 2a), and a linear ribbon for **2** along the  $a$  axis, just as if the  $\text{SCN}^-$  passed through every parallel Cu1–S1–Cu2 triangle plane (Figure 2b). In each  $[\text{Cu}_2(\text{SCN})(\text{pz})]_\infty$  chain of **1**, different chiral  $\text{Cu}^I$  atoms alternately appear, and all of the chains are the same. In contrast, in **2** only one type of chiral  $\text{Cu}^I$  atom appears in one  $[\text{Cu}_2(\text{SCN})(\text{pz})]_\infty$  chain, and another type of chiral  $\text{Cu}^I$  atom appears in the other  $[\text{Cu}_2(\text{SCN})(\text{pz})]_\infty$  chain. Therefore, there are two types of opposite chiral  $[\text{Cu}_2(\text{SCN})(\text{pz})]_\infty$  chains, each of which only contains one type of chiral  $\text{Cu}^I$  atom.

The binding of the Cu1 and N3 atoms between two adjacent  $[\text{Cu}_2(\text{bppz})]$  units produces two different infinite  $[\text{Cu}_2(\text{bppz})]_\infty$  chains, forming 2-fold helices for **1** with a screw axis along the  $b$  direction (Figure 3a) and meso helices for **2** with a screw axis along the  $c$  direction (Figure 3b). Each chain of the two isomers connects to the four neighboring chains through the Cu2 and N4 atoms, extending to a

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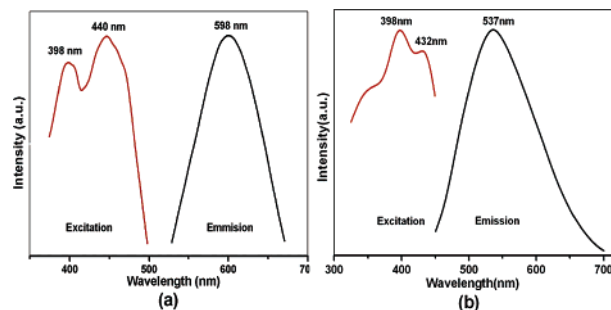
**Figure 4.** Polyknotted network with topology of  $(6^3)(6^8 \cdot 8 \cdot 10)$  for **1** (a) and  $(6^3)(6^6 \cdot 8^4)$  for **2** (b) derived from 2-fold interpenetrated  $10^3$ -a net (blue and red) and  $10^3$ -b net (blue and red) connected by a  $\text{SCN}^-$  anion bridge (green).

$3\text{D} [\text{Cu}_2(\text{bppz})]_\infty$  net. Interpenetration of two 3D nets leads to the  $[\text{Cu}_2(\text{bppz})]_\infty$  structures of the two isomers. It is noteworthy that in **1** the helical chains are of the same handedness and contain only one type of chiral  $\text{Cu}^I$  atom in one single  $3\text{D} [\text{Cu}_2(\text{bppz})]_\infty$  net and the opposite in the other net. As a result, the two interpenetrating nets are of opposite chirality, but as a whole, the molecule is a mesomer (Figure S2 in the Supporting Information). In **2**, all of the chains are the same and contain two types of chiral  $\text{Cu}^I$  atoms, and also the two interpenetrating nets are the same (Figure S3 in the Supporting Information).

In both isomers, thiocyanate units acting as bridging connectors cross-link the two interpenetrating nets, resulting in two inseparable  $3\text{D} [\text{Cu}_2(\text{bppz})]_\infty$  nets and whole polyknotted networks. However, the linkage modes, zigzag chains for **1** and linear ribbon for **2**, are different. As mentioned above, they are polyknotted isomers.

Topologically speaking, if the  $\text{pz}^-$  ring unit and the two doubly bridged  $\text{Cu}^I$  centers function as three- and five-connected nodes respectively, the two isomers can be abstracted into three and five binodal networks with the rarely encountered topology of  $(6^3)(6^8 \cdot 8 \cdot 10)$  for **1** (Figure 4a) and  $(6^3)(6^6 \cdot 8^4)$  for **2** (Figure 4b) (Wells notation<sup>11</sup>). In the two topological networks, provided that thiocyanates were ignored, then two three-connected uniform 2-fold interpenetrated networks,  $10^3$ -a net for **1** and  $10^3$ -b net for **2**, are presented, which are commonly found in a number of crystalline motifs.<sup>12</sup>

Therefore, the whole topological networks of the two isomers, taking the thiocyanate unit into consideration, can be described as the derivation from 2-fold interpenetrating



**Figure 5.** Solid-state excitation and emission spectra of **1** ( $\lambda_{\text{ex}} = 398$  and  $440$  nm (red);  $\lambda_{\text{em}}^{\text{max}} = 598$  nm (black)) and **2** ( $\lambda_{\text{ex}} = 398$  and  $432$  nm (red);  $\lambda_{\text{em}}^{\text{max}} = 537$  nm (black)) at room temperature.

$10^3$ -a and  $10^3$ -b nets cross-linked by connectors with different linkage modes (zigzag and linear). As mentioned above, the cross-linking will result in polyknotted networks and different linkage modes lead to polyknotted isomers.

Both isomers are very stable in air and began to decompose when heated to as high as  $360$  °C (Figure S5 in the Supporting Information). Interestingly, they exhibit strong photoluminescence in the solid state at room temperature (Figure 5). On the basis of the photoluminescence of other  $\text{Cu}^I$  compounds such as  $[\text{Cu}^I(\mu_2\text{-pyrazolate})]^{10\text{b,d,e}}$  and  $[\text{Cu}^I(\mu_2\text{-S})]^{13}$  type complexes, the emissions of the two isomers are ascribed to a mixture of ligand-to-metal charge transfer ( $\text{S} \rightarrow \text{Cu}$ ) and metal center  $3\text{d}^94\text{s}^1$  modified by a  $\text{Cu} \cdots \text{Cu}$  weak interaction.<sup>13,14</sup> Irradiation at the same wavelength gave rise to different emission bands, with that of **2** blue-shifted. The shift probably arises from a stronger  $\text{Cu} \cdots \text{Cu}$  interaction and  $\text{S}-\text{Cu}$  coordination bond because the distances of  $\text{Cu} \cdots \text{Cu}$  and  $\text{Cu}-\text{S}$  are shorter in **2** than in **1** (Figure 1).

In conclusion, two  $3\text{D}$  polyknotted topological polymers were obtained from a new ligand and  $\text{CuSCN}$  under different conditions. Both complexes are polyknotted topological isomers introduced by different linkage modes of the  $\text{SCN}^-$  anion between two interpenetrating  $10^3$  networks. Factors determining the formation of the two isomers and replacement of the  $\text{Cu}^I$  atom and  $\text{SCN}^-$  anion with other monovalence  $\text{d}^{10}$  metals and other bridging connectors and atoms will be further studied.

**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 synthetic procedures, powder X-ray diffraction, and thermogravimetric analysis data in PDF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC061152J

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