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

Shun-Ze Zhan, Dan Li,* Xiao-Ping Zhou, and Xin-Hui Zhou

Department of Chemistry & Multidisciplinary Research Center,
Shantou University, Guangdong 515063, People's Republic of China

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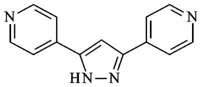
Two unprecedented 3D polyknotted isomers, arisen from different linkage modes of SCN^-, were obtained from 3,5-bis(4-pyridyl)-1*H*-pyrazole (Hbppz) and CuSCN under different conditions.

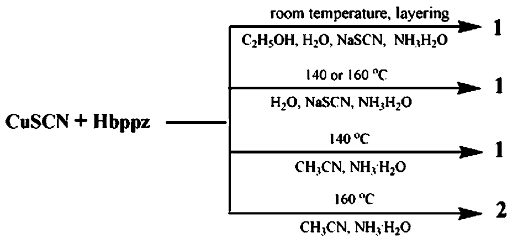
Supramolecular isomerism is an essential element in crystal engineering of coordination polymer frameworks because of not only their structural diversity but also their potential application.[1] Diversity of coordination modes, flexibility in ligands, and subtle environmental changes play some important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

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.[5] Different kinds of entangled supramolecular complexes, including interpenetration, polycatenation, polythreading, polyknotting, and so on, have been reviewed.[5] In these systems, a small number of coordination compounds exhibit polyknotted network architectures[6] that are built through the cross-linking of different types of interpenetrating networks by bridging connector ligands and by hydrogen-bonding/weak interactions.[5b] 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[1] though an enormous number of isomers are known in classical coordination chemistry.[1−4]

Chart 1. Structure of the Ligand Hbppz



Scheme 1. Synthesis of the Two Isomers



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[7] from 4-acetylpyridine and methyl isonicotinate as primary materials and was

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* To whom correspondence should be addressed. E-mail: dli@stu.edu.cn.

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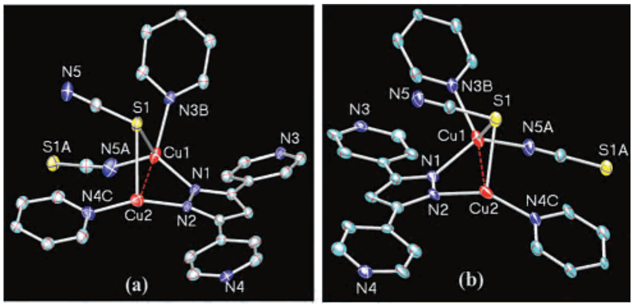

Figure 1. Coordination environments of the Cu atoms in **1** (a) and **2** (b). Selected bond distances (Å): **1**, Cu1−N1 1.972(3), Cu1−N3B 2.105(3), Cu1−N5A 1.928(4), Cu1−S1 2.585(1), Cu2−N2 1.903(3), Cu2−N4C 1.915(3), Cu2−S1 2.544(1), Cu1···Cu2 3.038(1); **2**, Cu1−N1 2.007(5), Cu1−N3B 2.085(5), Cu1−N5A 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).

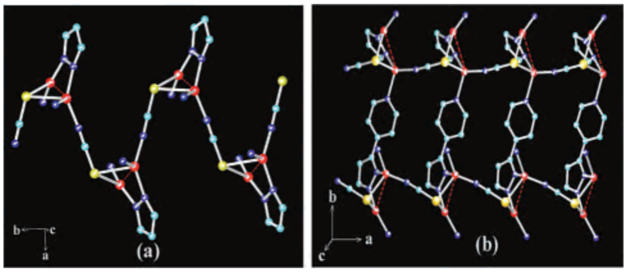

Figure 2. Zigzag and linear chains of $[\mathrm{Cu^I}_2(\mathrm{SCN})(\mathrm{pz})]_\infty$ in **1** (a) and **2** (b).

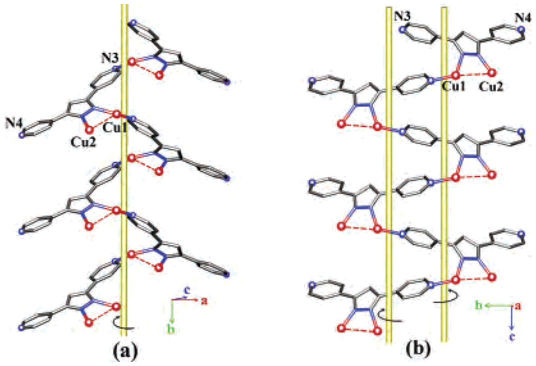

Figure 3. 2-fold helical (left-handed) and meso-helical chains of $[\mathrm{Cu^I}_2(\mathrm{bppz})]_\infty$ through Cu1 and N3 atoms in **1** (a) and **2** (b).

In isomers **1** and **2**,[8] $[\mathrm{Cu^I}_2(\mathrm{bppz})(\mathrm{SCN})]_\infty$, the deprotonated ligand bppz$^-$, as a tetradentate ligand bearing stronger binding ability than that in its neutral form, binds to four Cu atoms.[9] 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 μ_2 bridge[9,10] with the four atoms of N1, N2, Cu1, and Cu2 on a slightly distorted plane and a S atom of SCN− adopting a μ_2-S bridging mode, resulting in a familiar five-membered (S1−Cu1−N1−N2−Cu2) ring.[9b] 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 bppz$^-$ ligand, respectively. Furthermore, only the Cu1 atom is coordinated by the fourth N atom from another SCN$^-$. Therefore, a SCN$^-$ anion as a whole acts as a μ_3 bridge (μ_2-S and μ_1-N). It is clear that both four-coordinated Cu1 atoms 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 Cu$^{\mathrm{I}}$ complexes,[10] they are obviously shorter.

The main difference in both isomers is the bridging orientation of SCN$^-$ (Figure 1). In **1**, the 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 SCN$^-$ and pyrazolate in a trans-μ_2 mode (Figure 1a). However, in **2** they are doubly bridged in a cis-μ_2 mode (Figure 1b). Consequently, two quite different chains of $[\mathrm{Cu^I}_2(\mathrm{SCN})(\mathrm{pz})]_\infty$ come into being, zigzag chains for **1** along the *b* axis on the plane parallel with *a* and *b* axes, just as if the 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 SCN$^-$ passed through every parallel Cu1−S1−Cu2 triangle plane (Figure 2b). In each $[\mathrm{Cu^I}_2(\mathrm{SCN})(\mathrm{pz})]_\infty$ chain of **1**, different chiral Cu$^{\mathrm{I}}$ atoms alternately appear, and all of the chains are the same. In contrast, in **2** only one type of chiral Cu$^{\mathrm{I}}$ atom appears in one $[\mathrm{Cu^I}_2(\mathrm{SCN})(\mathrm{pz})]_\infty$ chain, and another type of chiral Cu$^{\mathrm{I}}$ atom appears in the other $[\mathrm{Cu^I}_2(\mathrm{SCN})(\mathrm{pz})]_\infty$ chain. Therefore, there are two types of opposite chiral $[\mathrm{Cu^I}_2(\mathrm{SCN})(\mathrm{pz})]_\infty$ chains, each of which only contains one type of chiral Cu$^{\mathrm{I}}$ atom.

The binding of the Cu1 and N3 atoms between two adjacent $[\mathrm{Cu^I}_2(\mathrm{bppz})]$ units produces two different infinite $[\mathrm{Cu^I}_2(\mathrm{bppz})]_\infty$ 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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(8) Crystal data for **1**: orthorhombic, space group *Pbca*, $M_r = 406.40$, $a = 12.3650(11)$ Å, $b = 7.8430(7)$ Å, $c = 28.896(3)$ Å, $V = 2802.3(4)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.927$ g·cm^{-3}, $F(000) = 1616$, $T = 293(2)$ K, 13 660 reflections collected, 2468 unique with $R_{\mathrm{int}} = 0.0342$, R1 [$I > 2\sigma(I)$] = 0.036, final (for all data) R1 = 0.0433, wR2 = 0.1012, GOF = 1.207. Crystal data for **2**: monoclinic, space group *Pc*, $M_r = 406.40$, $a = 5.6550(7)$ Å, $b = 15.4504(18)$ Å, $c = 8.1286(9)$ Å, $\beta = 97.531(2)°$, $V = 704.09(14)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.917$ g·cm^{-3}, $F(000) = 404$, $T = 293(2)$ K, 4354 reflections collected, 2190 unique with $R_{\mathrm{int}} = 0.0257$, R1 [$I > 2\sigma(I)$] = 0.0392, final (for all data) R1 = 0.0435, wR2 = 0.1056, GOF =1.132. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo Kα, $\lambda = 0.710\,73$ Å).

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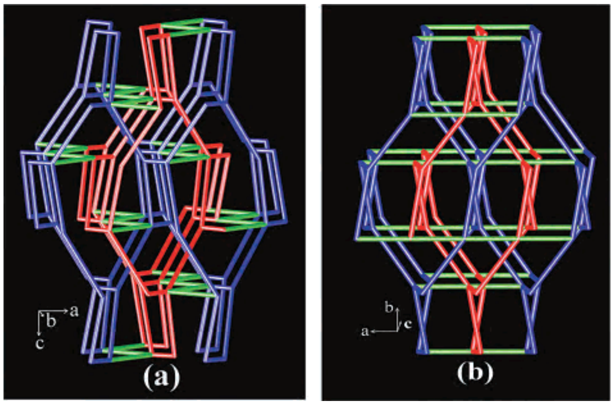

Figure 4. Polyknotted network with topology of $(6^3)(6^8{\cdot}8{\cdot}10)$ for **1** (a) and $(6^3)(6^6{\cdot}8^4)$ for **2** (b) derived from 2-fold interpenetrated 10^3-a net (blue and red) and 10^3-b net (blue and red) connected by a SCN^- anion bridge (green).

3D $[Cu^I_2(bppz)]_\infty$ net. Interpenetration of two 3D nets leads to the $[Cu^I_2(bppz)]_\infty$ 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 Cu^I atom in one single 3D $[Cu^I_2(bppz)]_\infty$ 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 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 3D $[Cu^I_2(bppz)]_\infty$ 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 pz^- ring unit and the two doubly bridged 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[11]). 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.[12]

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 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.

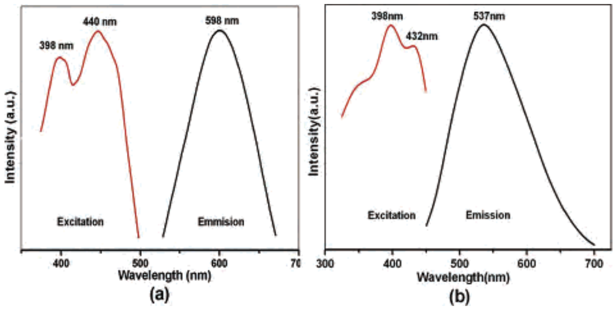

Figure 5. Solid-state excitation and emission spectra of **1** (a) [$\lambda_{ex} = 398$ and 440 nm (red); $\lambda_{em}^{max} = 598$ nm (black)] and **2** (b) [$\lambda_{ex} = 398$ and 432 nm (red); $\lambda_{em}^{max} = 537$ nm (black)] at room temperature.

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 Cu^I compounds such as $[Cu^I(\mu_2\text{-pyrazolate})]$[10b,d,e] and $[Cu^I\text{-}(\mu_2\text{-S})]$[13] type complexes, the emissions of the two isomers are ascribed to a mixture of ligand-to-metal charge transfer ($S \rightarrow Cu$) and metal center $3d^94s^1$ modified by a Cu···Cu weak interaction.[13,14] Irradiation at the same wavelength gave rise to different emission bands, with that of **2** blue-shifted. The shift probably arises from a stronger Cu···Cu interaction and S−Cu coordination bond because the distances of Cu···Cu and Cu−S are shorter in **2** than in **1** (Figure 1).

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

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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.

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