Coordination Polytubes with the Affinity for Guest Inclusion

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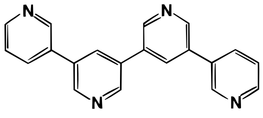
Despite numerous studies on porous coordination polymers, there still remains difficulty in predicting cavities in the polymer frameworks because of the frequent occurrence of interpenetration of the networks.[1,2] This problem can be, in principle, solved by designing organic ligands which disfavor the interpenetration. In this regard, the use of a panel-like ligand such as **1** is promising because its coordination assembly is expected to give polytube structures which have no possibility of interpenetration. Here we show that, upon treatment with a transition metal (CuI), ligand **1** assembles into polytube structures that accommodate organic guests in the tubular cavities. Interestingly, the polytube structures are templated by the guest molecules; that is, two polytubes possessing different connectivities with the guest-occupied volumes of ∼32 and 48%, respectively, have been obtained by using different organic guests. Ligand **1** has been recently shown to assemble into a molecular tube structure in solution with convergent (en)Pd^{2+} building block.[3]



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As a tetravalent and divergent building block, Cu_2I_2 component was employed in this study.[4] When ligand **1** was treated with CuI in CH_3CN solution, single crystals of the complex [**1**·(Cu_2I_2)]·2(CH_3CN)·H_2O (**2**) were formed.[5] The crystal structure of **2** revealed a 2D-polytube structure by the interconnection of the ligand **1** with Cu_2I_2 units. The conformation of ligand **1** in the network is helicated with interplanar angles, between adjacent pyridine rings, of 5.7°, 46.3°, and 44.9°. As a result, the polytube structure is more complicated than those expected from coplanar conformation. Three of the binding sites from each unit point inward, while the remainder point outward from the tube (Figure 1a). Each tube is self-assembled by six units of **1** (24 binding sites) and six units of Cu_2I_2 (24 binding sites). In effect, 18 Cu−N bonds are engaged in assembling one tube. The remaining 12 binding sites, six each from **1** and **2**, propagate the tube structure in two dimensions (Figure 1b).[6] The approximate diameter and length of the tube are 8 and 7 Å, respectively. The 2D layers pack on each other in the crystallographic *ab*-plane such that there is a channel formation along *c*-axis. In **2**, the guest molecules occupied 32% of the crystal volume.[7]

Interestingly, another polytube structure appeared when **1** was complexed with CuI in the presence of aromatic guests such as nitrobenzene (G_1) and cyanobenzene (G_2). Thus, single crystals of the complexes [**1**·(Cu_2I_2)]·2G_1 (**3**) and [**1**·(Cu_2I_2)]·2G_2 (**4**) were obtained by layering the acetonitrile solution of CuI on the corresponding guest solution of **1**.[8] The X-ray analysis showed that these polytubes accommodated relatively large guest molecules which induced a 3D-network. The guest molecules occupy 48% of the crystal volume (Figure 2a).

In both **3** and **4**, each polytube is comprised of a 1D-helical network along the crystallographic *a*-axis with the pitch length of 14 Å and with an approximate diameter of 10 Å (Figure 2b). These helices are formed by the interconnection of Cu_2I_2 units with the terminal and middle pyridines of **1** alternately. As a result each tube is formed by half of the binding sites, while the other half extends this tube network in the crystallographic *bc*-plane. The $-NO_2$ group of nitrobenzene in **3** is disordered over the two sites with 0.5 occupancy, whereas the cyanobenzene in **4** has been found without disorder in a noncentrosymmetric space group. Importantly, although the network is centrosymmetric, the arrangement of the poles of cyanobenzenes in one direction results in a non-centrosymmetric space group. The cyanobenzenes form a dimer via C−H···N (H···N: 2.383 Å; C···N; 3.197 Å; C−H···N 146.1°) hydrogen bonds, which is further sandwiched between two moieties of **1** via aromatic face−face interactions.[9] The

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[4] The Cambridge Structural Database analysis on the building block Cu_2I_2 when connected to four N-atoms resulted in seven compounds, but all of them form discrete species with chelated lingands. A network structure with a −Cl analogue: Yaghi, O. M.; Li, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 207.

[5] The single crystals of the complex **2** were prepared by layering the CH_3CN solution (10 mL) of CuI (0.098 g, 0.5 mmol) onto a $CHCl_3$ solution (20 mL) of **1** (0.31 g, 1.0 mmol). Crystal Data of **2**: Triclinic, $P\bar{1}$; $a = 9.715(1)$ Å, $b = 10.978(2)$ Å, $c = 13.880(2)$ Å, $\alpha = 84.976(3)°$, $\beta = 83.800(4)°$; $\gamma = 67.496(3)°$; $V = 1357.8(4)$ Å^3; $Z = 2$; $D_c = 1.936$ g cm^{-3}; 4437 unique reflections out of 5782 with $I > 2\sigma(I)$, final *R*-factors $R_1 = 0.056$; $wR_2 = 0.090$.

[6] For easy understanding of the whole structure, some stereoview presentations are given in Supporting Information.

[7] Spek, A. L. *PLATON; A Multi Purpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 1999.

[8] The single crystals of the complexes **3** and **4** were prepared by layering the CH_3CN solution (10 mL) of CuI (0.098 g, 0.5 mmol) onto the solution of **1** (0.31 g, 1.0 mmol) in the corresponding guest molecule (20 mL). Crystal Data of **3**: Monoclinic, *C*2/*c*, $a = 14.081(3)$ Å, $b = 14.413(3)$ Å, $c = 16.420(3)$ Å, $\beta = 97.814(4)°$, $V = 3301.4(12)$ Å^3, $Z = 4$, $D_c = 1.882$ g cm^{-3}, 3896 unique reflections out of 10046 with $I > 2\sigma(I)$, final *R*-factors $R_1 = 0.0429$; $wR_2 = 0.0568$. Solving the structure in *Cc* space group resulted in same disordered guest molecule as in *C*2/*c* space group. Crystal Data of **4**: Monoclinic, *Cc*, $a = 13.975(1)$ Å, $b = 14.563(1)$ Å, $c = 16.437(2)$ Å, $\beta = 98.576(2)°$, $V = 3307.7(5)$ Å^3, $Z = 4$, $D_c = 1.802$ g cm^{-3}, 5525 unique reflections out of 10383 with $I > 2\sigma(I)$, final *R*-factors $R_1 = 0.0314$; $wR_2 = 0.0669$. This structure was also solved and refined in the *C*2/*c* space group. However, it resulted in the disordered guest molecule but same *R*-value. All of the data were measured on a Siemens SMART/CCD diffractometer at 193 K. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at calculated positions and refined using a riding model.

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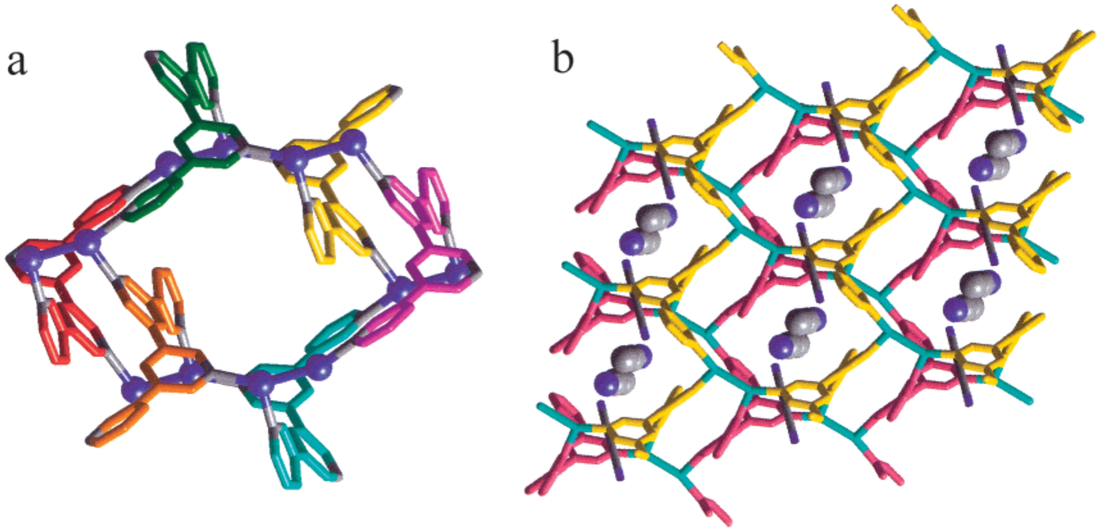

Figure 1. (a) Representation of one tube of the 2D-polytube in crystal structure of **2**. Each ligand is colored differently (blue = Cu and gray = N) and I atoms are removed for the sake of clarity. Please note the helical geometry of **1**. (b) Top view of the extended 2D-polytube in the crystal structure of **2**. Guest molecules presented in ball mode and cylinder mode (disordered). The top and bottom rims of the framework colored differently and Cu atoms are in turquoise.

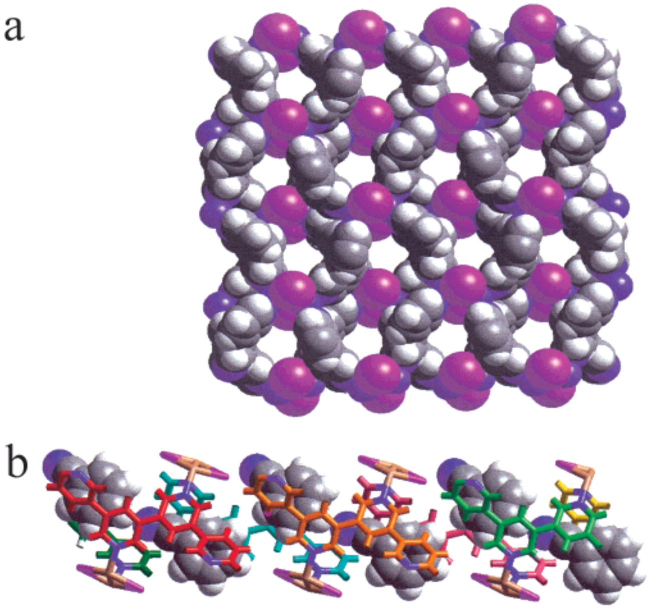

Figure 2. (a) Top view of the space filling drawing of the 3D-polytube in the crystal structure of **4** (blue = Cu, N; magenta = I; gray = C; and white = H). The channels are occupied by guest molecule. (b) Representation of the polytube that observed in the crystal structure of **4**. Each ligand is colored differently for the sake of clarity (light orange = Cu, blue = N, and magenta = I). The guest molecules are represented in solid mode. Please note the formation of C–H···N dimer of the guest molecules and panel like geometry of **1**.

formation of these dimers and the effective $\pi-\pi$ interactions with **1** by the guest molecules seems to be crucial factors for inducing the 3D-network, even in the presence of CH_3CN. For example, the presence of aniline, which cannot form dimers similar to the above guests, failed to induce a 3D-polytube and exclusively resulted in the single crystals of **2**.

The thermogravimetric analysis on the complex **4** indicated that the guest was liberated at 145 °C (23% weight loss) and the network sustained its integrity up to 300 °C. The integrity of the network after guest removal was confirmed by the FT-IR and powder X-ray: FT-IR spectrum of the guest removed sample was identical with that of the original sample except the absence of the gust absorption bands and the powder X-ray showed strong diffraction pattern even after removal of the guest molecule.[1a,b]

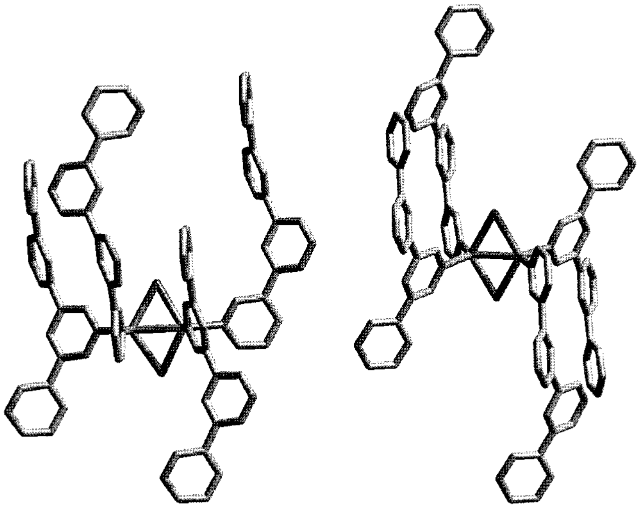

Figure 3. The basic building blocks of **2** (left) and **4** (right).

Some interesting features are found by comparing the structures of the 2D-network (**2**) and the 3D-network (**3** or **4**). Although the network topologies are completely different, the coordination environment of the basic building blocks of **2** and **3** or **4** is the same (Figure 3). In the building block of 3D-network the binding sites of **1** are evenly distributed (six on each side) on both sides of Cu_2N_4 plane. In contrast, binding sites in 2D-network are distributed unevenly: three binding sites on one side and nine binding sites on the other side of Cu_2N_4 plane. In both complexes, the Cu atoms have distorted tetrahedral coordination geometry. The Cu_2I_2 unit is noncoplanar in **2** with the I–Cu–I–Cu torsion angle of 30°, whereas it is coplanar in **3** and **4** with the I–Cu–I–Cu torsion angle of 0°. The Cu–Cu and Cu–I distances ranges between 2.56 and 2.64 Å and 2.64 and 2.70 Å, respectively.

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Supporting Information Available: Tables of crystal structure refinement data, positional parameters, bond lengths and angles, spectra of IR, powder diffraction and TG-analysis, and some stereoviews of the structures are available through the Web only (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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