A Novel Noninterpenetrated Open Framework Structure with Extraordinarily Large Cavity Sizes: A New Coordination Polymer Containing a Rigid and Bent Molecular Building Block

Dong Mok Shin, In Su Lee, and Young Keun Chung*
School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-747, Korea

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A new coordination polymer is prepared from $Co(SCN)_2$ and 1,3-bis(*trans*-4-styrylpyridiyl)benzene and characterized by X-ray diffraction studies, which shows a noninterpenetrated framework structure containing extraordinarily large cavities and channels.

The construction of new coordination polymer networks through the rational combination of organic ligand 'spacers' and metal 'nodes' is an area of intense current interest.[1] In particular, open framework networks of coordination polymers have been studied exclusively because of their unique applications to molecular sieving or separation, selective catalysis, selective chemical sensor, and optoelectronics.[2,3] Networks of coordination polymers are influenced by several factors such as the structure of ligands, coordination preference of metal ions, coordination behavior of counterions, and the solvent system. Among these factors, the chemical structure of organic ligands plays an extremely important role in dictating polymer topology.

Much research effort has been concentrated on the exploitation of rod-like rigid ligands such as pyrazine and 4,4′-dipyridine in the construction of a remarkable class of materials containing diverse architectures such as square-grids, brick walls, bilayers, and herringbones.[4] However, relatively few reports deal with the use of bent ligands with a rigid molecular angle other than 180 °.[5] In this report we describe the remarkable structure of a coordination polymer made from 1,3-bis(*trans*-4-styrylpyridiyl)benzene (**1**) and $Co(SCN)_2$. The assembly of **1** with $Co(SCN)_2$ afforded a noninterpenetrated framework structure (**2**) containing extraordinarily large cavities and channels.

Compound **1**,[6] in which the two nitrogen donors are about 12.5 Å apart and the angle between the N-donor and lone-pair is fixed at 120 °, was chosen as a ligand. When a solution of $Co(SCN)_2$ in MeOH was layered onto a solution of **1** in nitromethane (or dichlorometahne) and stood for several days, single crystals suitable for X-ray analysis were grown on the interface of the two solutions.[7] The formulation of **2** was confirmed by a single-crystal X-ray diffraction method and elementary analysis. The X-ray structural analysis of **2**[8] reveals the formation of 2-dimensional open framework structure (Figure 1).

A view depicting the metal ion coordination in **2** is shown in Figure 2. Cobalt centers are in a compressed octahedral environment with four long Co–N (pyridine) bonds and two short Co–N (NCS) bonds and there are no significant differences between the two crystallographically independent cobalt centers. The ligand of **1** adopts a nearly planar molecular structure, and symmetrically bridges two cobalt centers with inter-metal distances of 17.04 Å and 16.33 Å. In this way, two different types of nano-sized cavities (A and B) are formed.

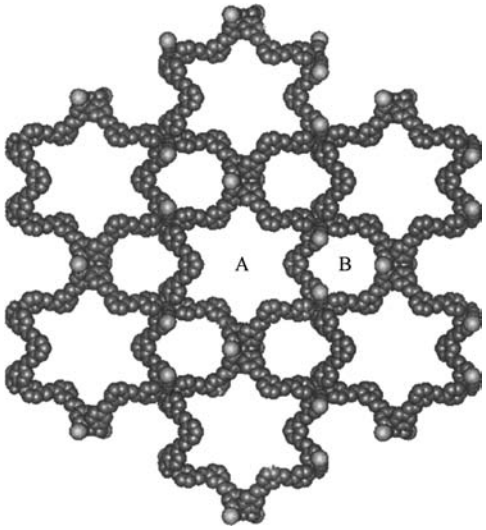

Figure 1. The 2-dimensional open framework network in **2**. Two different types of cavities of A and B existing in the 2-D network.

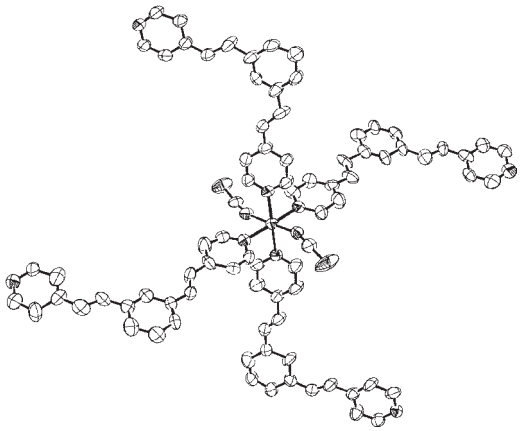

Figure 2. Ortep drawing of the cobalt ion coordination environment in **2**.

Figure 1 reveals the puckered David's star shape of the cavity A and the bowl-like shape of cavity B. The cavity A is isostructural with the metallacalix[6]arene motif found in $[Cu(2\text{-hydroxypyrimidine})_2]_\infty^+$ structure[5] such that six cobalt centers are occupying each corners of a hexagon and six **1** ligands are bridging them with a 1,3,5-alternative arrangement. Its cavity size is uncommonly large such that the metal-metal distances through the diagonal are 32.67 Å and 34.09 Å and the shortest diagonal distance of the cavity is 21.90 Å. The cavity of B consists of three cobalt nodes and three molecules of **1** bridging them and

has a bowl-like structure. The distances between the cobalt center and the nearest carbon of the phenyl rings at the opposite side are 17.32 and 19.02 Å. The edges of cavities A and B are shared with each other and in this way 2-dimensional layers with open framework structure are extended along the (3 0 4) plane.

Besides the formation of large cavities, another interesting feature of this structure is the packing of layers that form the channel structure. For framework structures with a large cavity size, it is common for interpenetration or catenation to fill the void.[9] In spite of the existence of large cavities, the 2D layers of **2** are noninterpenetrated and stacked with neighboring layers along the c axis. In such a way, the cavities are aligned and slanted to form 1D channels (Figure 3). Each channel has an identical repeating unit consisting of one A cavity and two B cavities. The breadth of the channel is 10.48 Å in *a* axis and 13.31 Å in *b* axis and the effective size of the channel is 11.77 × 8.42 Å. Since the coordination polymer **2** is electrically neutral, there are no counteranions occupying the channel region. This suggests that most of the channel region is occupied by disordered solvent molecules and accessible by other guest molecules.[10] Any attempts to include metal ions or organic molecules into the cavities were not successful.

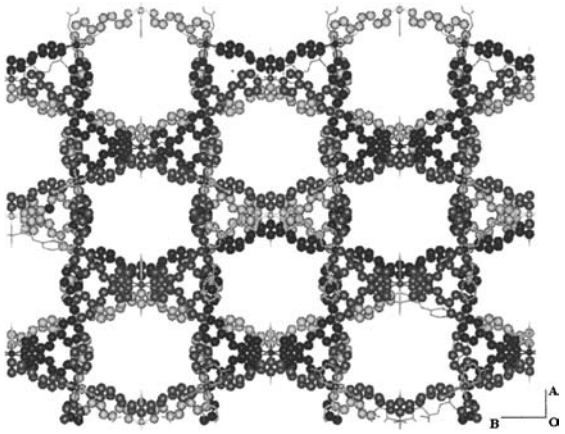

Figure 3. View showing the 1-D channel along the c axis.

Disappointingly, the stability of the crystal is not high enough to prevent it losing its crystallinity and it turns opaque upon removal of solvate molecules. Further characterization of the porosity, rigidity, and stability of the framework remains to be conducted.

In summary, we have synthesized a new coordination polymer with nano-sized cavities and channels using a new framework structural module that utilizes large, rigid, and bent organic ligands as a spacer building block. Noninterpenetrated neutral networks with such large cavities are rare.

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7 0.050 g (0.29 mmol) of $Co(SCN)_2$ in 5 ml of MeOH was layered onto the solution of 0.16 g (0.57 mmol) of **1** in 5 ml of nitromethane and stood for several days to give 0.15 g (0.20 mmol) of single crystals of **2** (70%). Anal. Found: H, 4.44; C, 66.20; N, 10.96; S, 8.08%. Calcd for **2**•CH_3OH: H, 4.68; C, 66.57; N, 10.83; S, 8.26%.

8 Single crystal X-ray data were collected on an Enraf-Nonius CCD single crystal X-ray diffractometer at room temperature using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97), and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were treated as idealized contributions. Crystal data for **2**. $C_{63}H_{48}Co_{1.50}N_9S_3$ (293 K). M = 1115.68, monoclinic, space group C2/m, a = 19.868(1), b = 32.659(1), c = 15.036(1), β = 119.879(3), V = 8459.4(7) Å^3, Z = 4, $\rho_{calc.}$ = 0.876 g/cm^{-3}, absorption coefficient = 0.404 mm^{-1}, total reflections collected 15999, unique 9423 (R_{int} = 0.0773), GOF = 1.056, R_1 = 0.0948, R_w = 0.2240 ($I > 2\sigma(I)$). Crystallographic data (excluding structure factors) for **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 177955. Copies of the data can be obtained free of charge in application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

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