

Novel Nanoporous Coordination Polymer Sustained by Self-Assembly of T-Shaped Moieties

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The recent surge in research devoted to coordination polymers was spawned by a fundamental interest in the development of new approaches to the prediction of crystal structures and has subsequently been fueled by the practical opportunities that are offered by new classes of functional materials. In the context of the former, it is clear that even the simple strategy of propagating transition metals with linear bifunctional ligands¹ affords an array of new network architectures, many of which do not exist in natural solids. “Clay mimics”² or “zeolite mimics”³ have the gross structural and functional features of their naturally occurring analogues but are based upon very different chemical components, and most importantly, they are inherently modular⁴ and therefore fine-tunable. In this paper we describe the remarkable structure of a new but anticipated⁵ supramolecular isomer⁶ of $[\text{Co}(4,4'\text{-bipyridine})_{1.5}(\text{NO}_3)_2]_n$, **1**.

The monomeric unit of **1** represents a simple and prototypal example of a “T-shape” module. Such modules have thus far produced four structurally distinct supramolecular isomers: ladder (1D),^{6,7} brick wall (2D),^{7a} bilayer (2D),^{3d,6,8} and frame (3D)⁹ (Scheme 1). Two of these supramolecular isomers, ladder^{7b} and bilayer⁸ structures, have been exhibited by **1** using different crystallization conditions and guests. However, if **1** is crystallized via intermediate pyridine complexes, a dramatically different 3D supramolecular isomer is obtained (Scheme 1E).¹⁰ Figure 1 reveals how **1**·1.5 benzene exists as an open framework coordination polymer with remarkably large cavities and channels (effective cross-section of ca. 8×40 Å). This particular supramolecular isomer is to our knowledge unprecedented. However, it was suggested by Wells⁵ and can be regarded as being a structural isomer of the brick wall supramolecular isomer illustrated in Scheme 1B. The geometry, around the metal centers is consistent

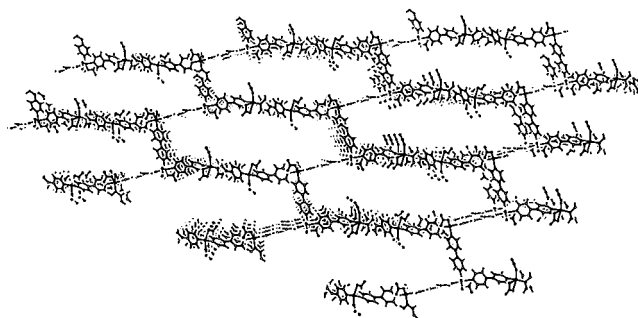
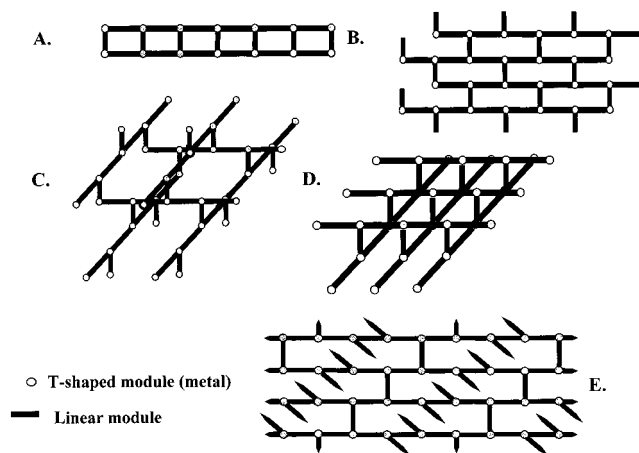


Figure 1. View of a cross-section of a single framework of **1**·1.5 benzene. Effective dimensions across the cavity are approximately 8×40 Å. The geometry around the metal atoms is roughly trigonal bipyramidal with 4,4'-bipyridine ligands occupying the vertexes of the T: Co–N (axial) 2.128(10)–2.162(10) Å; Co–N (equatorial) 2.055(10), 2.141(10) Å; Co–O (monodenate) 2.011(9), 2.031(10) Å; Co–O (bidentate) 2.174(9)–2.201(10) Å.

Scheme 1. Five Supramolecular Isomers that Have Been Observed for Self-Assembly of T-shape Modules: Ladder (A), Brick Wall (B), 3-D Frame or “Lincoln Logs” (C), Bilayer (D), Modified Brick Wall (E)



with distorted trigonal bipyramidal geometry and there are no significant differences between the two independent cobalt centers. However, unlike the previous supramolecular isomers of **1**, in which both nitrate ligands are symmetrically bidentate, one of

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(10) Crystals of **1**·1.5 benzene were prepared as follows: A solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.873 g, 3.0 mmol) and pyridine (0.32 mL, 4.0 mmol) in 10 mL of MeOH was layered onto a solution of 4,4'-bipyridine (0.624 g, 4.0 mmol) in 10 mL of benzene. After standing overnight under ambient conditions, the reaction vessel was placed in an ice bath. This resulted in two types of crystals, colored violet and peach, respectively. The violet crystals, **1**·1.5 benzene, are stable for approximately 1 h in the absence of mother liquor and do not melt below 300 °C. Crystal data: $[\text{Co}(4,4'\text{-bipyridine})_{1.5}(\text{NO}_3)_2]_n \cdot 1.5(\text{benzene})$, monoclinic, Cc , $a = 21.4382(13)$ Å, $b = 23.3175(12)$ Å, $c = 10.7981(6)$ Å, $\beta = 110.113(10)^\circ$, $V = 5068.6(5)$ Å³, $Z = 8$, $D_c = 1.401$ mg/m³, 5195 reflections out of 6749 with $I > 2\sigma(I)$ were measured on a Siemens SMART/CCD diffractometer at 203 K, final R -factors $R1 = 0.0619$, $wR2 = 0.1625$. Non-hydrogen atoms were refined anisotropically. Benzene guest molecules were refined as rigid hexagons with a C–C distance of 1.39 Å, and thermal parameters were allowed to refine anisotropically. Hydrogen atoms were fixed at calculated positions and refined using a riding model. The structure was also refined in centrosymmetric space groups $C2/c$ and $I2/a$. However, disordered guest molecules and relatively high R -factors were obtained. The peach-colored crystals are of different stoichiometry, $[\text{Co}(4,4'\text{-bipyridine})_2(\text{NO}_3)]_n$, and consist of infinite square grids with three molecules of benzene per metal atom (orthorhombic, $a = 30.5408(19)$ Å, $b = 11.4138(7)$ Å, $c = 30.5408(19)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 7836.1$ Å³). Similar compounds are described in ref 3. Square grids only are obtained with four molecules of guest per metal atom if *o*-xylene is used instead of benzene (tetragonal, $a = b = 16.1951(10)$ Å, $c = 17.9784(11)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 4715.3(8)$ Å³).

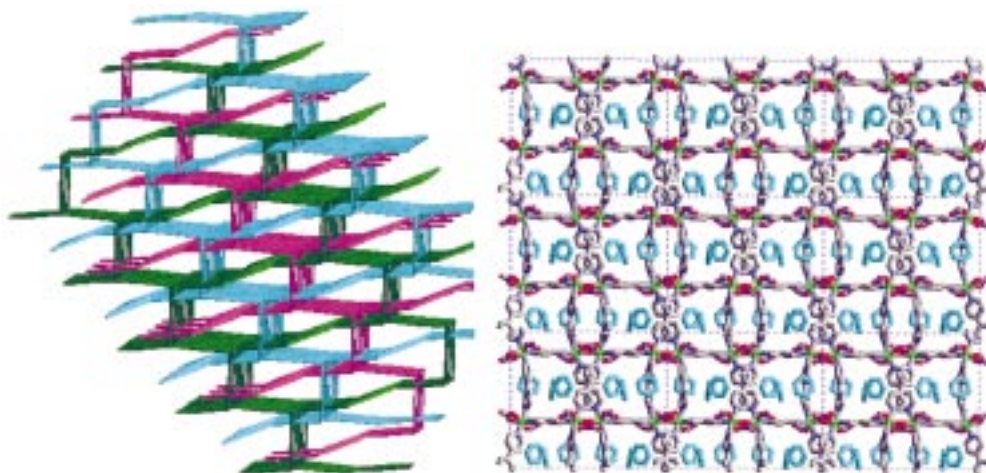


Figure 2. (a) Illustration of how the frameworks in **1**·1.5 benzene interpenetrate. The three independent frameworks are colored blue, green, and magenta, respectively. (b) A view of the crystallographic *ab* plane that illustrates the microchannels that lie parallel to the crystallographic *z*-axis. Benzene guest molecules are blue. The diagonal distance across the microchannels is 12.9 Å meaning that the effective cross-sectional area is ca. 9 Å × 9 Å.



Figure 3. Benzene–benzene interactions in the microchannels of **1**·1.5 benzene. The benzene molecules also interact with the walls of the microchannels.

the nitrate ligands in **1**·1.5 benzene is bidentate, whereas the other is monodentate.

The networks in **1**·1.5 benzene exhibit a 3-fold level of interpenetration¹¹ (Figure 2a). However, despite this interpenetration, there exist large channels parallel to the crystallographic *z*-axis (Figure 2b). These channels contain an ordered chain of benzene molecules which is inherently chiral because of its supramolecular structure. On the basis of a molecular volume for benzene of ca. 125 Å³, the benzene molecules are found to represent ca. 30% of the volume of the crystal. A portion of one of the benzene chains is illustrated in Figure 3 and reveals that the expected¹² stacking interactions occur between benzene molecules and that the chains are inherently polar. However, the geometry of the interactions is quite different from the idealized T-shape or edge-to-face interactions observed in the crystal structure of benzene.¹³ Interestingly, the coordination polymer network contains a pseudo-inversion center, but the benzene chains are aligned in such a manner that the crystal structure is noncentrosymmetric.

There are a number of salient features concerning the structure of **1**·1.5 benzene. First, the critical importance of crystallization conditions upon the structure of covalent coordination polymers is further¹⁴ highlighted by the fact that **1**·1.5 benzene represents the fifth motif observed for a simple T-shaped module and the

third supramolecular isomer of **1**. All three supramolecular isomers of **1** are based upon the same asymmetric unit. Interestingly, only modestly different crystallization conditions have thus far been employed, crystals being grown via layering MeOH solutions of Co(NO₃)₂·6H₂O onto solutions of ligand and guest, to observe such diversity of structure. It therefore seems likely that the guest molecules have a templating effect (chloroform and acetone sustain ladders, and CS₂ sustains a bilayer). It further seems reasonable to relate the existence of such supramolecular isomerism to the phenomenon of polymorphism¹⁵ in molecular crystals. Second, we are unaware of any other crystallographically characterized framework with one of its dimensions as large as the one reported herein. Unfortunately, the full potential for porosity is precluded by the 3-fold interpenetration. Nevertheless, solvent still accounts for ca. 30% of the crystal volume. Finally, we note that the crystal structure of **1**·1.5 benzene is polar although the host framework and individual guest molecules are inherently centrosymmetric. Whereas there are examples of chiral host frameworks that are generated from achiral modules,¹⁶ we are unaware of other examples of high symmetry guests that generate chiral aggregates and thereby impart bulk polarity to centrosymmetric host frameworks. This aspect of crystal engineering has many potentially interesting implications for materials science since such features are extremely rare in naturally occurring open framework solids and have not been encountered in zeolites.

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Supporting Information Available: Tables of crystal structure refinement data, positional parameters, bond lengths and angles (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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