

## BRIEF COMMUNICATION

# A Novel Coordination Polymer with an Interwoven Double-Layer Structure: Synthesis and Characterization of $[\text{Zn}(4,4'\text{-bipy})(\text{H}_2\text{O})(\text{SO}_4)] \cdot 0.5\text{H}_2\text{O}$

Songping D. Huang<sup>1</sup>, Ren-Gen Xiong, and Pura H. Sotero

*Department of Chemistry and Center for Materials Research and Characterization, University of Puerto Rico, San Juan, Puerto Rico 00931*

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The *pseudo* three-dimensional coordination polymer  $[\text{Zn}(4,4'\text{-bipy})(\text{H}_2\text{O})(\text{SO}_4)] \cdot 0.5\text{H}_2\text{O}$  (**1**) was synthesized by the ethanothermal reaction of 4,4'-bipyridine with  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in the molar ratio of 1:1 in a sealed tube at 120°C. The compound was characterized by FT-IR, diffuse reflectance UV/vis, X-ray powder diffraction, and single crystal X-ray analysis. The structure features two-dimensional interwoven networks stacked together by the complementary hydrogen bonding between layers. Crystallographic data for **1**,  $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_{5.5}\text{SZn}$  are monoclinic  $C2/c$  ( $\neq 15$ ),  $a = 20.545(1)$ ,  $b = 9.6492(6)$ ,  $c = 12.3949(8)$  Å,  $\beta = 104.089(1)^\circ$ ,  $V = 2383.3(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.921$  g cm<sup>-3</sup>,  $\mu = 2.260$  mm<sup>-1</sup>,  $T = 295$  K,  $R = 0.0310$ ,  $R_w = 0.0398$ , and goodness-of-fit = 1.663. © 1998 Academic Press

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It has been shown that the use of 4,4'-bipyridine or pyrazine as linear  $T_2$  tectons (**1**) along with suitably chosen metal ions can lead to the spontaneous formation of infinite one- (1-D), two-(2-D), and three-dimensional (3-D) frameworks by molecular self-assembly (2–6). Because of their robust and crystalline structures with well-defined stoichiometries, intrinsic tailorability and synthetic simplicity, coordination polymers have emerged as new materials with unique chemical and physical properties. These materials bridge the gap between molecular and solid state chemistry. Of particular interest are the 2-D and 3-D structures with pores comparable to those found in some zeolites (7). In addition to the host–guest chemistry, the potential applications of such metal–organic microporous materials may

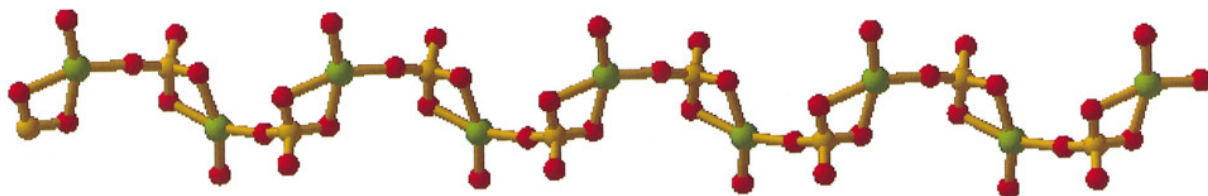
range from separations (8), ion exchange (6(a)), and shape-selective catalysis (3(b)) to ordered matrices for nonlinear optical (NLO) chromophores (9).

We have launched a research program aimed at exploring the use of two or more different organic/inorganic tectons to create novel coordination polymers. In this report, we describe the synthesis and characterization of a *pseudo*-three-dimensional coordination polymer  $[\text{Zn}(4,4'\text{-bipy})(\text{H}_2\text{O})(\text{SO}_4)] \cdot 0.5\text{H}_2\text{O}$  (**1**) consisting of interwoven double layers. The compound was formed between the linear  $T_2$  4,4'-bipyridine and the coordinate  $\text{SO}_4^{2-}$  anion. The latter acts as a tecton with unusual topology.

The reaction of 4,4'-bipyridine with  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in ethanol in the molar ratio 1:1 in a sealed tube at 120°C for 2 days gave **1** as a pure crystalline product in 77% yield (13). The compound is insoluble in common organic solvents such as THF, acetone,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_3\text{CN}$  or water. The single crystal X-ray structure analysis showed that **1** crystallizes in the space group  $C2/c$  ( $\neq 15$ ) (10). The asymmetric unit contains a  $\text{Zn}^{2+}$  ion, a 4,4'-bipy ligand, a coordinated  $\text{H}_2\text{O}$  molecule, a  $\text{SO}_4^{2-}$  anion, and half a crystallization water situated on the inversion center. The  $\text{Zn}^{2+}$  ions are first coordinated by the  $\text{H}_2\text{O}$  molecules and linked by the  $\eta^1, \eta^2, \mu_2\text{-SO}_4^{2-}$  anions to form a one-dimensional  $[\text{Zn}(\text{H}_2\text{O})(\text{SO}_4)]_n$  chains (see Fig. 1). The metal centers in the  $[\text{Zn}(\text{H}_2\text{O})(\text{SO}_4)]_n$  chains have distorted square planar coordination and alternate in two different directions at a dihedral angle of  $49.9(1)^\circ$  between the adjacent  $\text{ZnO}_4$  planes. When such metal centers are further connected with the rod-like 4,4'-bipy molecules, the neighboring linkages run across each other at an angle approximately corresponding to the above-mentioned dihedral angle. Figure 2 depicts the one-dimensional across-running  $[\text{Zn}(4,4'\text{-bipy})]_n^{2+}$  chains. The compound possesses two-dimensional interwoven networks of double layers as shown in Fig. 3. In addition, each coordinated water molecule forms strong

<sup>1</sup>To whom correspondence should be addressed. Fax: (787)-281-7349. E-mail: huang@zintl.chem.uprr.pu.

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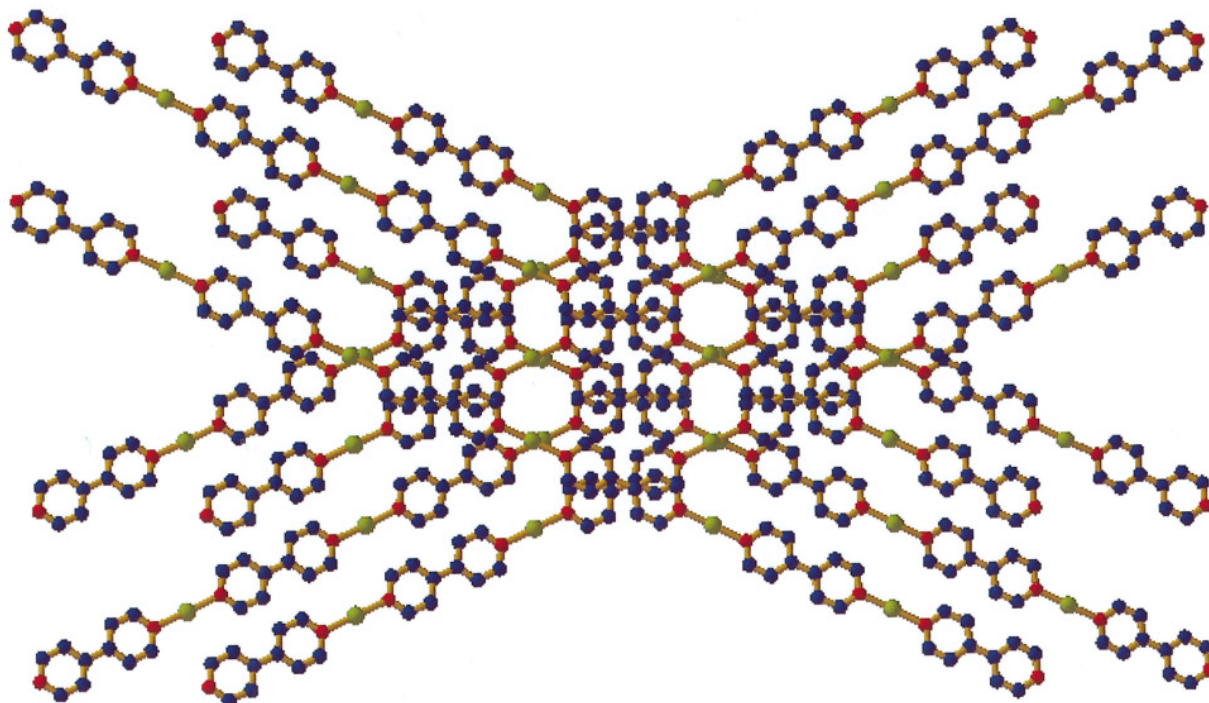


FIG. 1. The one-dimensional  $[\text{Zn}(\text{H}_2\text{O})(\text{SO}_4)]_n$  chain. Color code: green = zinc, yellow = sulfur, and red = oxygen.

FIG. 2. The cross-running one-dimensional  $[\text{Zn}(4,4'\text{-bipy})]_n^{2+}$  chains.

hydrogen bonds with the two oxygen atoms in the sulfate anion from the adjacent layer (i.e.,  $\text{O}(5)\text{--O}(1) = 2.744(3)$  and  $\text{O}(5)\text{--O}(2) = 2.719(3)$  Å). Figure 4 shows such complementary hydrogen bonding between two layers. Thus, the compound is actually *pseudo* three-dimensional. The most common coordination modes of the  $\text{SO}_4^{2-}$  anion are monodentate, bidentate, and  $\mu_2$ - and  $\mu_3$ -bridging (11). To the best of our knowledge, **1** is the first example of the  $\text{SO}_4^{2-}$ -containing compounds to show the  $\eta^1$ ,  $\eta^2$ ,  $\mu_2$ -coordination.

It should be noted that when weakly or noncoordinating anions such as  $\text{ClO}_4^-$  or  $\text{NO}_3^-$  are used, the metal-4,4'-bipyridine complexes will form 1-D, 2-D, 3-D structures consisting of metal-ligand square grids (2–6). However, **1** possesses an unprecedented structural motif for such complexes because of the unusual coordination of the  $\text{SO}_4^{2-}$  anion. In this sense, the novel structure of **1** is formed as a result of the strong structural directing force of this anion.

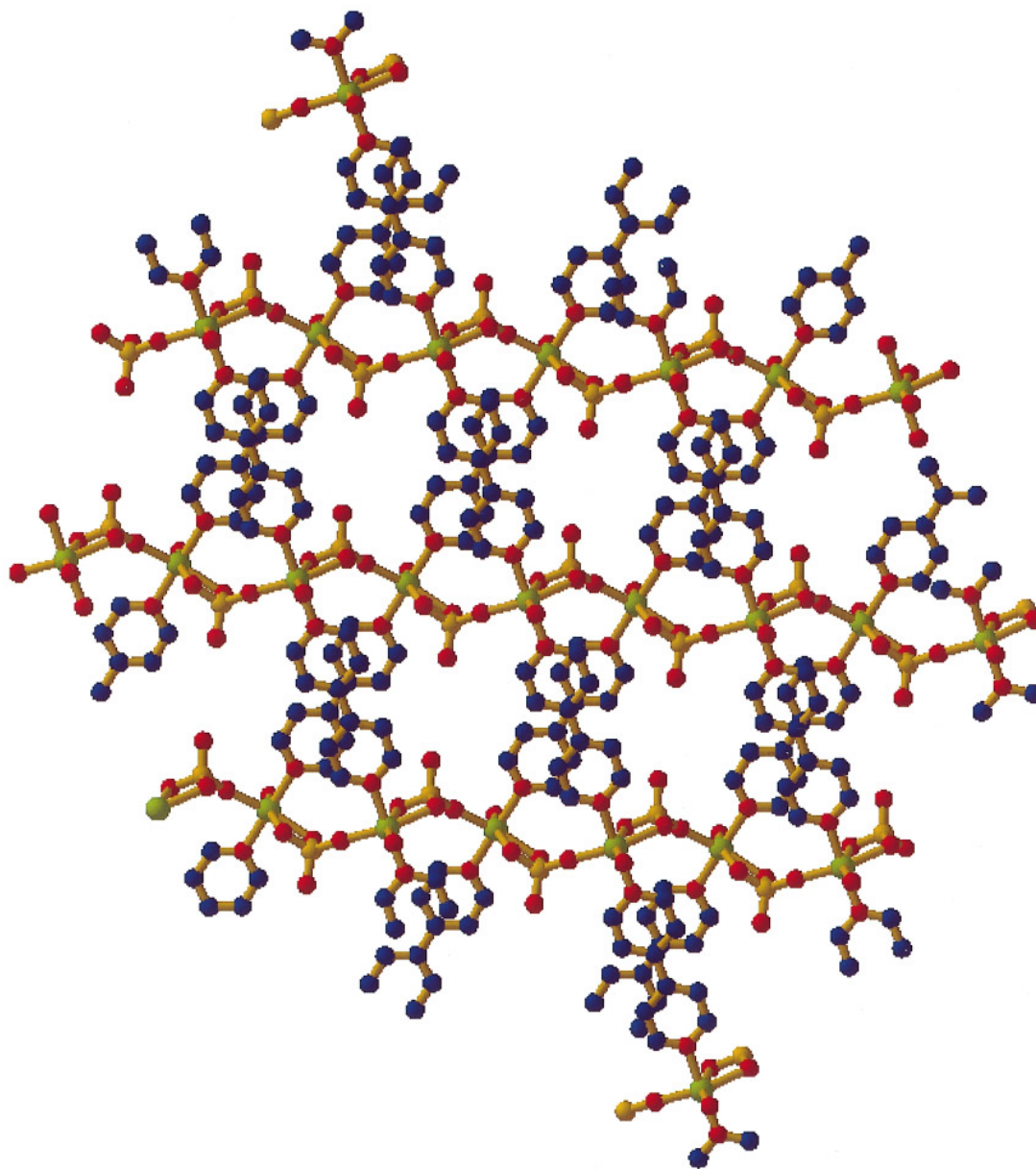


FIG. 3. The two-dimensional interwoven  $[\text{Zn}(4,4'\text{-bipy})(\text{H}_2\text{O})(\text{SO}_4)]$  network.

In the diffuse reflectance UV/VIS spectrum, **1** shows a broad band at  $\sim 280$  nm, an absorption essentially identical to that of free 4,4'-bipyridine, and can be considered optically transparent in the entire visible region. The characteristic mid-IR bands include a strong and very broad peak at  $1115\text{ cm}^{-1}$  and a medium peak at  $1066\text{ cm}^{-1}$  attributable to the coordinate  $\text{SO}_4^{2-}$  ions. In addition, the aromatic C–C and C–N stretching vibrations appear at  $1610$  (s, sh),  $1535$  (m, sh),  $1486$  (m, sh), and  $1417$  (s, sh)  $\text{cm}^{-1}$ . The product was examined by X-ray powder diffraction to ensure phase purity. The observed X-ray powder diffraction patterns of the

bulk materials match well with those calculated from the X-ray single-crystal data.

In conclusion, we have synthesized and structurally characterized a *pseudo*-three-dimensional coordination polymer  $[\text{Zn}(4,4'\text{-bipy})(\text{H}_2\text{O})(\text{SO}_4)] \cdot 0.5\text{H}_2\text{O}$ . The formation of such material seems to represent a new approach to designing and constructing unprecedented solids; i.e., different tectons can be used in combination to create novel structural motifs. This may open up a new avenue to a potentially large class of coordination polymers.

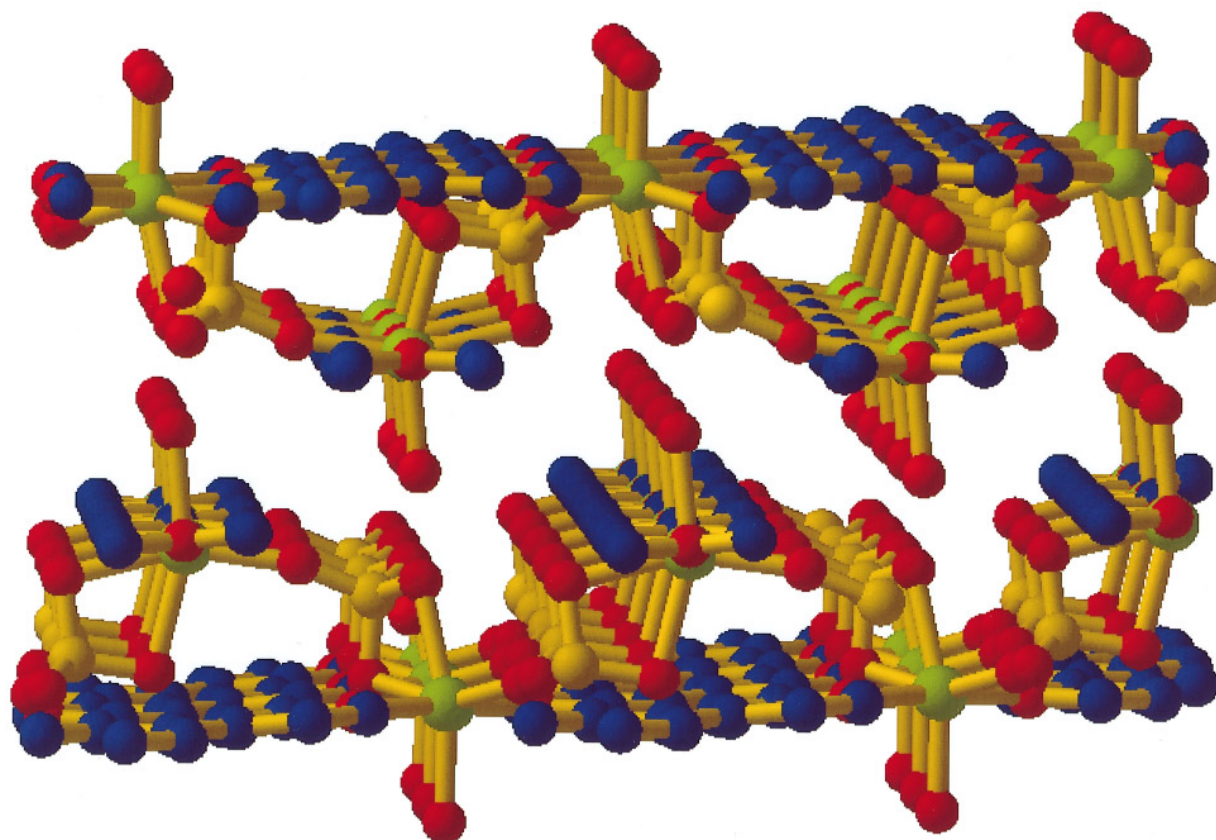


FIG. 4. The complementary hydrogen bonding between two  $[\text{Zn}(4,4'\text{-bipy})(\text{H}_2\text{O})(\text{SO}_4)]$  layers.

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- Crystallographic data for **1**,  $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_{5.5}\text{SZn}$ , monoclinic  $C2/c$  (#15),  $a = 20.545(1)$ ,  $b = 9.6492(6)$ ,  $c = 12.3949(8)$  Å,  $\beta = 104.089(1)^\circ$ ,  $V = 2383.3(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calc}} = 1.921$  g cm<sup>-3</sup>,  $\mu = 2.260$  mm<sup>-1</sup>,  $T = 295$  K. Structure solution and refinement based on 2097 reflections with  $I_0 \geq 3.0\sigma(I_0)$  converged at  $R = 0.0310$ ,  $R_w = 0.0398$ , and goodness-of-fit = 1.663. Data were collected on a Siemens SMART diffractometer using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). An empirical absorption correction based upon simulated  $\psi$  scans was applied to the data set.
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