

T-Shaped Molecular Building Units in the Porous Structure of $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$

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Received October 12, 1995

The successful assembly of extended frameworks from molecular building units has yielded a remarkable class of materials having diverse architecture and functions.¹ These include metal–organic solids with open frameworks having zeolite-like attributes² and others having important electronic³ and magnetic⁴ properties. One of the simplest strategies employed in the production of such 3-D networks is schematically illustrated in Figure 1a,b, where open-framework diamond-like networks have been achieved by the addition copolymerization of either rod-like ligands^{5a–c} or metal clusters with tetrahedral metal ions.^{2c,5d,e} In this report, we show how the tendency of silver(I) for linear coordination may be exploited^{5f,g} in its reaction with the rod-like 4,4'-bipyridine (4,4'-bpy) ligand to form extended chains that cross-link yielding a 3-D open framework having $23 \times 6 \text{ \AA}$ extended channels as shown in Figure 1c. The hydrothermal synthesis, structure, and porosity of crystalline $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$ will be described.

A mixture of AgNO_3 (0.050 g, 0.29 mmol) and 4,4'-bpy (0.050 g, 0.32 mmol) was suspended in 5 mL of deionized water and transferred to a stainless steel bomb, which was sealed, heated at 140 °C for 5 h, and then cooled gradually to 110 °C for 3 h, followed by further cooling to 90 °C for 4 h prior to being cooled down to room temperature. Large, pale gray parallelepiped crystals of $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$ were collected, washed with deionized water and ethanol, and then air-dried to give 0.083 g (86% yield based on silver nitrate).^{6,7} This compound is stable indefinitely in air, and it is insoluble in water and polar and nonpolar organic solvents such as benzene,

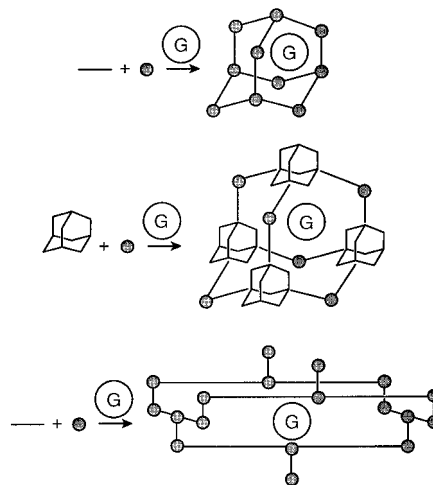


Figure 1. A schematic representation of the assembly of metal ions (dark spheres) and organic ligands (dark rods) or metal tetrahedral clusters to yield diamond-like frameworks (a, top, and b, middle) or open frameworks with rectangular channels (c, bottom). In each case the assembly is accompanied by the inclusion of a guest molecule G which occupies the voids.

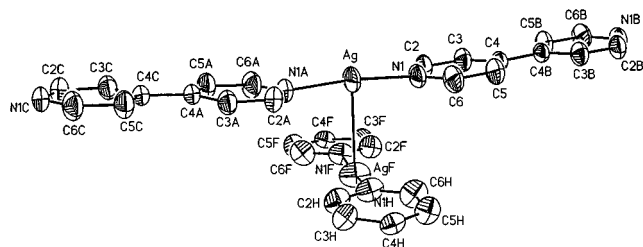


Figure 2. The building block unit including the asymmetric unit present in crystalline $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$ with non-hydrogen atoms represented by thermal ellipsoids drawn to encompass 50% of their electron density. Atoms labeled with additional letters A–H are symmetry equivalent to those atoms without such designation. The hydrogen atoms have been omitted for clarity.

hexane, diethyl ether, methanol, ethanol, acetonitrile, nitromethane, and acetone.

X-ray structure determination⁸ on a single crystal isolated from the reaction mixture was performed to reveal an extended open cationic network composed of the building unit shown in Figure 2. Each silver(I) is linked to two nitrogens of different but symmetry-equivalent 4,4'-bpy units in a nearly linear coordination [$\text{N1–Ag–N1A} = 173.7(2)^\circ$] to form extended chains. Adjacent chains are cross-linked in an almost perpendicular fashion [$\text{N1–Ag–AgF–N1F} = 81.0(2)^\circ$] by Ag–Ag bonds leading to a 3-D open network as represented in Figure 3a.⁹ The overall structure is composed of three such networks that interpenetrate¹⁰ to give an open framework having 23×6

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(5) Frameworks having the motifs shown in Figure 1a–c have been synthesized. For example: (a) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, 117, 6273–6283. (b) Subramanian, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 2127–2129. (c) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, 116, 1151–1152. (d) MacGillivray, L. R.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325–1326. (e) Yaghi, O. M.; Sun, Z.; Richardson, D. A.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, 116, 807–808. (f) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, 117, 7287–7288. (g) Yaghi, O. M.; Li, G. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 207–209.

(6) Anal. Calcd for $\text{AgC}_{10}\text{H}_8\text{N}_2\text{O}_3$: C, 36.83; H, 2.47; N, 12.89; Ag, 33.08. Found: C, 36.64; H, 2.53; N, 12.93; Ag, 33.12. FTIR (KBr, 1600–460 cm^{-1}): 1608 (s), 1541 (w), 1494 (w), 1421 (m), 1386 (vs), 1365 (s), 1336 (s), 1228 (m), 1143 (w), 1076 (w), 1046 (w), 1011 (w), 824 (m), 807 (m), 731 (w), 643 (m), 614 (w), and 464 (w).

(7) The homogeneity of the bulk product was confirmed by comparison of the observed and calculated X-ray powder diffraction patterns. The calculated pattern was produced using the SHELXTL-XPOW program with the single-crystal data.⁸

(8) Single crystals of $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$ were analyzed at $20 \pm 1^\circ \text{C}$: Orthorhombic, space group $Fddd\text{-}D_{2h}^{24}$ (No. 70) with $a = 9.914(2) \text{ \AA}$, $b = 34.488(7) \text{ \AA}$, $c = 12.963(3) \text{ \AA}$, $V = 4432(2) \text{ \AA}^3$, $Z = 16$, $d_{\text{calcd}} = 1.955 \text{ g}\cdot\text{cm}^{-3}$, and $\mu_a(\text{Mo K}\alpha) = 1.82 \text{ mm}^{-1}$. A total of 1282 independent absorption-corrected reflections having $2\theta(\text{Mo K}\alpha) < 55.0^\circ$ (the equivalent of 1.0 limiting Cu K α spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (1.00° -wide) ω scans and graphite-monochromated Mo K α radiation. The structure was solved using “direct methods” techniques with the Siemens SHELXTL-PC software package as modified at Crystalytics Company. The resulting structural parameters have been refined to convergence [R_1 (unweighted, based on F) = 0.033 for 950 independent absorption-corrected reflections having $2\theta(\text{Mo K}\alpha) < 55.0^\circ$ and $I > 3\sigma(I)$] using counter-weighted, full-matrix, least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The nitrate anion appears to be statistically disordered in the lattice about the crystallographic C_2 axis which passes through the nitrogen atom N₂.

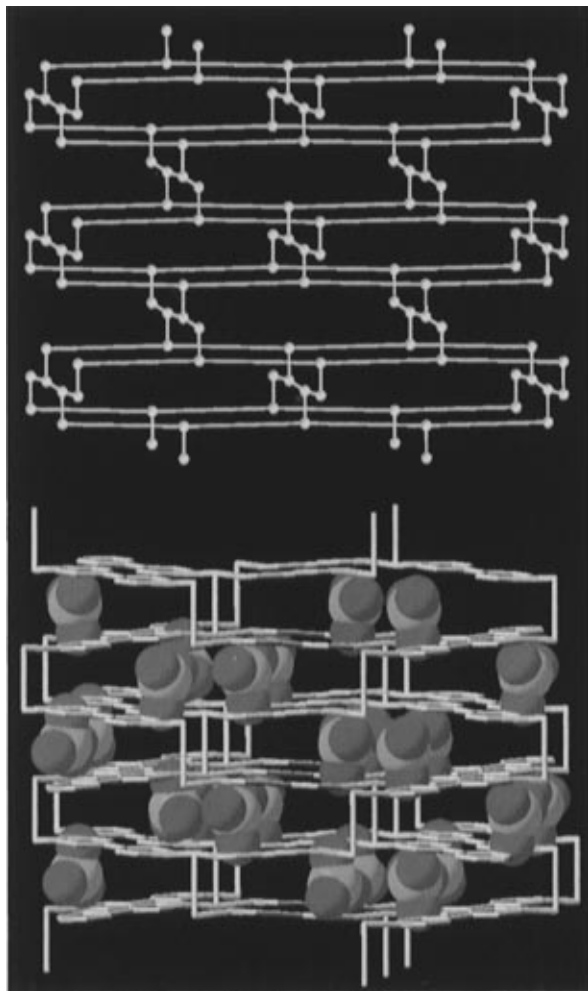


Figure 3. (a, top) A single framework of the $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$ structure shown here along the crystallographic direction [100]. Silver atoms are represented as yellow spheres and 4,4'-bpy as lines running horizontally across the page and almost vertically into the page, while Ag–Ag bonds are running vertically along the page. (b, bottom) The crystal structure of $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$ shown approximately down the crystallographic direction [100], where large channels which are occupied by nitrate anions exist in spite of the presence of three interpenetrated frameworks. The framework atoms are represented as lines: Ag, yellow; C, gray; N, light blue. The nitrate inclusions are statistically disordered about the crystallographic C_2 axis. Only one orientation is depicted with large spheres: O, red; N, green. The 4,4'-bpy hydrogens were omitted for clarity.

Å channels running along the [100] crystallographic axis where the nitrate ions reside (Figure 3b). The T-shaped silver coordination leaves an open coordination site pointing toward

the center of the channels. The nitrate guests form very weak interactions to the silver by binding to the vacant site (through the oxygens) in a *trans* fashion to the Ag–Ag bonds with Ag–O = 2.78(1) and 2.83(2) Å, which are typical of ionic interactions in metal nitrates.¹¹

Experimentation aimed at evaluating the ion exchange properties of this material showed that reversible exchange can be achieved. In a typical experiment, the addition of a slight excess of $\text{NaPF}_6(\text{aq})$ to a suspension of crystalline $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$ in water at room temperature showed that the NO_3^- anions begin to exchange with PF_6^- anions after 30 min, as evidenced by the infrared data. Here, intense PF_6^- bands at 835 and 560 cm^{-1} begin to appear as those intense bands from 1385 to 1335 cm^{-1} due to NO_3^- begin to disappear, with the rest of the spectrum remaining virtually unchanged. On the basis of FT IR data and elemental microanalysis¹² it is estimated that after 6 h nearly 95% exchange has occurred. Inspection of the crystals under an optical microscope during the exchange process revealed that the crystals became opaque upon complete exchange; however, they still give a sharp X-ray powder diffraction pattern. This pattern is not coincident with that of the original unexchanged material. We observed that, upon the addition of $\text{KNO}_3(\text{aq})$ to the exchanged solid, the transparency of the crystals is restored and their corresponding XRD pattern is found to be indistinguishable from that of the original starting solid, $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$. Analogous results were achieved for the reversible exchange of MoO_4^{2-} , BF_4^- , and SO_4^{2-} anions. The thermal stability of the $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$ network was investigated by performing thermal gravimetric analysis on a 25.894 mg sample which revealed no weight loss up to 238 °C. An abrupt but clean weight loss of 66% corresponding to one 4,4'-bpy and one nitrate per formula unit (theoretical 67%) was observed at 300 °C, leaving behind metallic silver.

At the outset of this study interpenetration had precluded the formation of open frameworks with accessible channels that are amenable to reversible inclusion chemistry. This work demonstrates the feasibility of achieving large channels having shapes yet unobserved in zeolites and other metal–organic porous frameworks in spite of the presence of interpenetrating frameworks. The T-shaped building unit which is responsible for the assembly of this 3-D open framework has the unique character of providing a vacant coordination site on the metal, a desirable property which has been implicated as the key structural feature causing activation of small molecules over metal oxides.¹³ Current investigations take into account the rarity of T-shaped coordination in porous materials and focus on accessing other solids that are based on this motif.

Acknowledgment. Financial support of this work by the Hoechst Celanese Corporation and the Petroleum Research Fund, administered by the American Chemical Society (PRF No. 28175-G3), is gratefully acknowledged. We thank Professor M. O'Keeffe for invaluable discussions and Ms. E. Houseman for providing assistance with producing Figure 1.

Supporting Information Available: Crystallographic data for $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$ including crystal structure analysis reports and tables of intensity collections, positional parameters, thermal parameters, and interatomic distances and angles (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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