

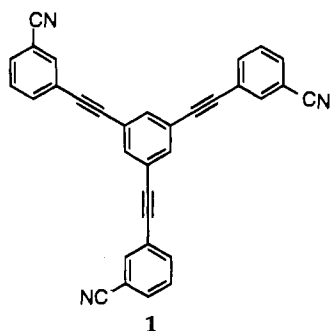
Zeolite-like Behavior of a Coordination Network

D. Venkataraman,[†] Geoffrey B. Gardner,[‡]
Stephen Lee,^{*,‡} and Jeffrey S. Moore^{*,†}Departments of Chemistry and
Materials Science & Engineering
University of Illinois, Urbana, Illinois 61801
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109-1055

Received August 14, 1995

Reversible removal and reabsorption of guests in solids without collapse of cages or channel structures, while well-known in materials such as zeolites, is a much less common phenomenon in molecularly-derived crystals.^{1–5} Typical molecular inclusion compounds irreversibly lose crystallinity, undergo a phase change,⁶ or alter their morphology^{6,7} upon loss of their guests. It has recently been shown, however, that some coordination or hydrogen-bonded networks can rapidly exchange inclusions or counterions while maintaining crystal integrity.^{8–13} Even so, removal of guest species in these systems without simultaneous replacement by a substitute apparently leads to destruction of the host lattice.¹⁴ The development of molecularly-based materials that are stable to the loss of inclusions represents an important step toward a new class of microporous substances. Here we report the structure and behavior of a coordination network that reversibly loses and reabsorbs guest species without undergoing a change in phase or morphology.

The addition of silver triflate to tritopic ligand **1** in benzene at room temperature results in a white precipitate. Heating this

**1**

mixture to 100 °C in a sealed tube, followed by slow cooling,

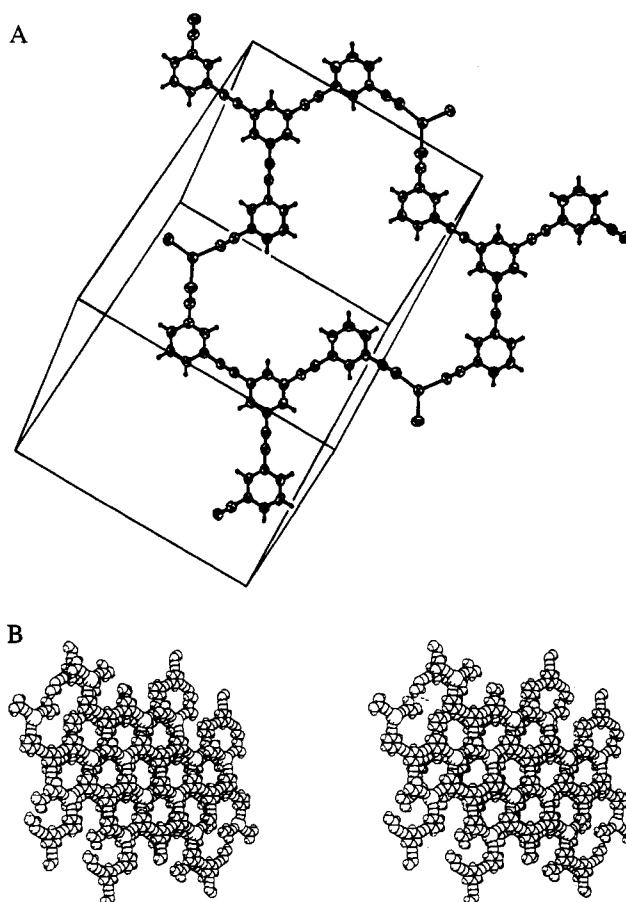
[†] University of Illinois.[‡] University of Michigan.(1) Barrer, R. M. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, pp 191–248.(2) Powell, H. M.; Wetters, B. D. P. *Chem. Ind.* **1955**, 256–7.(3) Allison, S. A.; Barrer, R. M. *J. Chem. Soc. (A)* **1969**, 1717–23.(4) Cartraud, P.; Cointot, A.; Renaud, A. *J. Chem. Soc., Faraday Trans. 1* **1981**, 77, 1561–7.(5) MacNicol, D. D. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 2, pp 1–45.(6) McAdie, H. G. *Can. J. Chem.* **1962**, 40, 2195–2203.(7) Knight, H. B.; Witnauer, L. P.; Coleman, J. E.; Noble, W. R. J.; Swern, D. *Anal. Chem.* **1952**, 24, 1331–4.(8) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, 112, 1546–54.(9) Mahdyarf, A.; Harris, K. D. *J. Chem. Soc., Chem. Commun.* **1993**, 51–3.(10) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, 116, 1151–2.(11) Wang, X.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1994**, 116, 12119–20.(12) Gardner, G. B.; Venkataraman, D.; Moore, J. S.; Lee, S. *Nature* **1995**, 374, 792–5.(13) Endo, K.; Sawaki, T.; Koyanagi, M.; Kobayashi, K.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1995**, 117, 8341–52.(14) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, 369, 727–9.

Figure 1. X-ray crystal structure of coordination network **2**. (A) ORTEP (50% probability) of a single layer showing the simplest cyclic motif of the 2D planar network. The included solvent molecules and triflate counterions have been omitted for clarity. (B) Stereoview down [101] showing the space-filling model of four different layers and the resulting channels. Benzene molecules that occupy the space in the channels are omitted for clarity.

yields single crystals suitable for X-ray diffraction.^{15–17} The structure of the resulting solid ($[\text{Ag} \cdot (\mathbf{1})(\text{CF}_3\text{SO}_3)] \cdot 2\text{C}_6\text{H}_6$, **2**)¹⁸ is a three-connected,¹⁹ two-dimensional coordination network (Figure 1A). The coordination geometry around silver is trigonal pyramidal, with three nitriles of the network in the basal plane and a triflate counterion in the apical position. The simplest cyclic motif of the network is a [12]annulene-like segment. The sheets are stacked in an $\cdots\text{ABCD}\cdots$ sequence, creating channel structures that run at an oblique angle to [101], i.e., the layer normal (Figure 1B). The framework occupies only 43% of the total volume of the unit cell. Difference Fourier analysis locates 16 molecules of benzene per unit cell in the channels (2 mol of benzene/mol of **1**), four of which are disordered.²⁰

(15) Crystal and refinement data for **2**: 0.53 mm × 0.38 mm × 0.36 mm, colorless prism, $\text{C}_{46}\text{H}_{24}\text{AgF}_3\text{N}_3\text{O}_3\text{S}$, $M = 863.61$, monoclinic, $I2/a$, $a = 17.720(2)$ Å, $b = 19.067(2)$ Å, $c = 24.680(2)$ Å, $\beta = 103.88(2)^\circ$, $V = 8095.1(14)$ Å³, $Z = 8$, $\rho = 1.417$ Mg/m³, $\mu = 0.607$ mm⁻¹. Single crystal diffraction data were collected on an Enraf-Nonius CAD-4 at 293 K using Mo K α ($\lambda = 0.71073$ Å) radiation. The structure was refined by full-matrix least-squares on F_o^2 (data/restraints/parameters: 6321/1/480), converging to $R1 = 0.0581$, $wR2 = 0.1356$ (on 3397, $I > 2\sigma(I)$ observed data); $R1 = 0.1474$, $wR2 = 0.1855$ (all data).

(16) Sheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–73.(17) Sheldrick, G. M. *A Crystal Structure Solution Program*; Institute für Anorg. Chemie, Göttingen, Germany, 1993.(18) Satisfactory analytical data ($\pm 0.3\%$ C, H, N) were obtained.(19) Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: New York, 1993; pp 63–140.

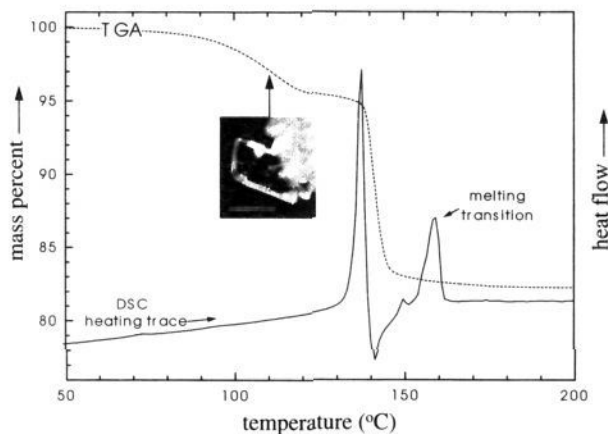


Figure 2. Overlay of TGA and DSC traces, each recorded at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Also included is an optical micrograph of a single crystal of **2** at room temperature in reflected light after the crystal was heated to $110\text{ }^{\circ}\text{C}$ for 10 min (bar equals $100\text{ }\mu\text{m}$).

The TGA trace of **2** (Figure 2) reveals two discrete mass losses at $110\text{ }^{\circ}\text{C}$ and $145\text{ }^{\circ}\text{C}$, corresponding to a mass percent of 4 and 12 benzene molecules, respectively. DSC (Figure 2) and optical microscopy indicate no evidence of a phase change associated with the first mass loss. At $145\text{ }^{\circ}\text{C}$, a solid-to-solid phase transition occurs concomitant with the loss of the remaining benzene molecules. This phase eventually undergoes a melting transition at $169\text{ }^{\circ}\text{C}$. No chemical decomposition is observed up to $200\text{ }^{\circ}\text{C}$.

The unit cell parameters of a single crystal of **2** heated to $110\text{ }^{\circ}\text{C}$ for 10 min and subsequently cooled to room temperature remain unchanged within the standard deviation of the original crystal. TGA experiments on crystals of similar or larger dimensions confirm that a mass loss equivalent to 4 benzene molecules occurs under these conditions. These crystals remain optically transparent (Figure 2) and uniformly birefringent when viewed between crossed-polarizers. Powder X-ray diffraction on bulk samples shows that the original crystalline phase is stable to the heat treatment ($110\text{ }^{\circ}\text{C}$ for 10 min). The observed changes in diffraction intensity upon heating are in agreement with the calculated changes in the simulated powder pattern upon removal of the disordered benzene from the single crystal model of **2** (see supporting information). This result supports the notion that the first TGA mass loss is associated with the removal of disordered benzene. The stability of **2** toward partial loss of its guests is in distinct contrast to the behavior of inclusion compounds, which generally undergo a change in phase and morphology when the guests leave the host.⁶

(20) The SQUEEZE routine in the program PLATON indicates no residual solvent spaces. Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578–9.

Upon cooling the melt, exothermic transitions are observed by DSC for samples contained within hermetic pans, while no transitions are observed if the pans are left open. These observations suggested that reabsorption of benzene might be possible in solids which have had their included guests removed. Indeed, microcrystalline samples heated to $145\text{ }^{\circ}\text{C}$ under vacuum and subsequently cooled to room temperature reabsorb benzene vapor in an amount that corresponds to the mass percent in the original, unheated sample (see supporting information). Sorption saturation is achieved in $\sim 60\text{ h}$ at room temperature. X-ray powder diffraction shows that the original solid phase was reformed. This behavior is analogous to that of classical inclusion compounds.²¹ In contrast, samples of **2** heated to $110\text{ }^{\circ}\text{C}$ reabsorb benzene in an amount equivalent to 4 molecules of benzene in less than 45 min without ever undergoing a phase change.

The findings reported here lend further support to the concept of molecularly-based zeolites. Future experiments will investigate sorption kinetics and selective guest uptake by this complex as a function of its phase state.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-94-23121) and the U.S. Department of Energy through the Materials Research Laboratory at the University of Illinois (Grant DEFG02-91-ER45439). A portion of this research was carried out at the Center for Microanalysis of Materials, University of Illinois, which is supported by the U.S. Department of Energy under Grant DEFG02-91-ER45439. J.S.M. acknowledges support from the 3M Co. and the Camille Dreyfus Teacher-Scholar Awards Program. S.L. thanks the J. D. and C. T. MacArthur Foundation (1993–97) and the A. P. Sloan Foundation (1993–95) for fellowships. We thank the School of Chemical Sciences, Materials Chemistry Laboratory at the University of Illinois, for single crystal X-ray data collection.

Supporting Information Available: Synthesis of **1**, crystallization conditions for **2**, DSC traces on cooling molten **2**, single crystal rotation photograph of **2** after heating to $110\text{ }^{\circ}\text{C}$, a series of TGA traces recorded after exposing benzene-free samples of **2** to benzene vapor at room temperature for the different times, observed and simulated powder diffraction patterns of **2** before and after heating, powder diffraction data of **2** after heating to $145\text{ }^{\circ}\text{C}$ and subsequent exposure to benzene vapor for 6 h, table of crystal data and structure refinement for **2**, and tables of bond angles and bond lengths for **2** (19 pages); calculated and observed structure factors for **2** (29 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.

JA9527661

(21) McAdie, H. G.; Frost, G. B. *Can. J. Chem.* **1958**, *36*, 635–51.