

Ru₆ Triangular Molecular Assembly

Solid-State Supramolecular Organization of Supermolecules into a Truly Molecular Zeolite**

Kom-Bei Shiu,* Hong-Chan Lee, Gene-Hsiang Lee,
Bao-Tsan Ko, Yu Wang, and Chu-Chieh Lin

Both inorganic zeolites and organic zeolitelike solids are attracting intense interest currently because of their functional properties.^[1] However, in contrast to many network porous materials with permanent porosity after partial or total removal of guests,^[2] zero-dimensional (i.e. discrete) analogues are scarce in the literature.^[3] The inherent difficulty in stabilizing such a material arises from the lack of structural rigidity, from its low thermal stability, and from the close-packing requirement of the molecular entities to minimize the Gibbs free energy by filling the voids in the structure.^[4] Herein, we present a truly molecular zeolite with both

structural rigidity and suitable thermal stability. The formation of this solid through cooperative self-assembly of unique triangular-tube organometallic supermolecules in both solution and the solid state is apparently driven positively by the close packing requirement in the molecular crystals. This material contains two types of 1D channels that are filled with solvent guests. However, the rigid nature of the solid architecture not only allows the complete removal of the molecular guests at ambient temperature without collapse of framework, but also has high thermal stability. Interestingly, the water molecules adsorbed into the microporous material also increase its thermal stability.

The treatment of [Ru₃(CO)₁₂] with 4,4'-biphenyldicarboxylic acid, followed by the addition of PPh₃, produced eclipsed-[[Ru₂(CO)₄(PPh₃)₂](μ-4,4'-O₂CC₆H₄C₆H₄CO₂)₃ (**1**).^[5] Complex **1** is air-stable when solid and readily soluble in acetone and CH₂Cl₂, indicative of molecular aggregates in the solid state. Indeed, as determined by single-crystal X-ray crystallography at 150 K, the crystal structure of **1** consists of discrete molecules in a shape of an equilateral-triangle shaped tube (Figure 1). The single crystals, grown from CH₂Cl₂/

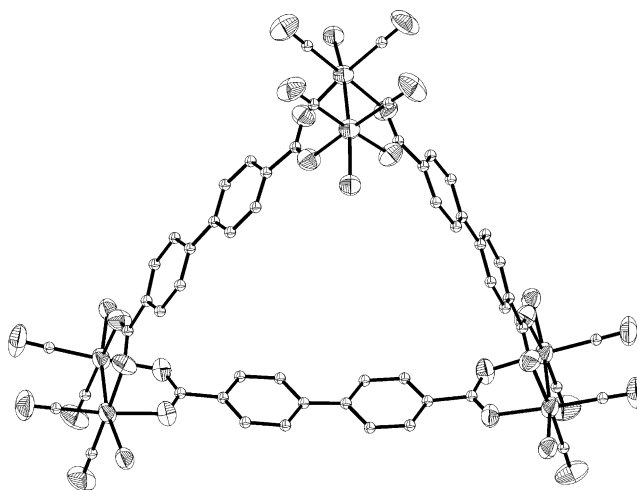


Figure 1. Triangular-tube supermolecule, **1** (ORTEP plot, thermal ellipsoids at the 50% probability level). All phenyl groups and hydrogen atoms are omitted for clarity.

MeOH, were found to contain many solvent guests are present (Figure 2). The six bonded phosphane ligands, which are situated on the rims of two tube openings, do not close the tube but allow guests to move in and out. The triangle edge, which has a length of 15.340(1) Å, is defined by the midpoints of the Ru–Ru bonds, whereas the depth of the tube is determined approximately by the Ru–Ru bond length (about 2.7 Å).

Molecules of **1** were packed in a hexagonal closest packing (hcp) arrangement with alternating ABAB layers. Except for the guest molecules, each lattice contains two molecular units: one unit in the A layer is symmetrically related by a screw 6₃ axis to another in the B layer (Figure 2 and 3). A noncovalent association between the phenyl groups of the phosphane, attracted through edge-to-face π–π stacking interactions^[6] can also be observed (Figure 3). Interestingly, apart from

[*] Prof. Dr. K.-B. Shiu, H.-C. Lee
Department of Chemistry
National Cheng Kung University
Tainan City 701 (Taiwan)
Fax: (+886) 6-274-0552
E-mail: kbshiu@mail.ncku.edu.tw

G.-H. Lee, Prof. Dr. Y. Wang
Instrument Center
National Taiwan University
Taipei 106 (Taiwan)

B.-T. Ko, Prof. Dr. C.-C. Lin
Instrument Center
National Chung-Hsing University
Taichung 402 (Taiwan)

[**] This work was supported by the National Science Council of the Republic of China for financial support of this research (Contract No. NSC89-2113-M006-019 and NSC90-2113-M006-021). We thank Prof. Dr. H. Teng of Chemical Engineering Department of National Cheng Kung University for measuring the BET area of the molecular zeolite.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

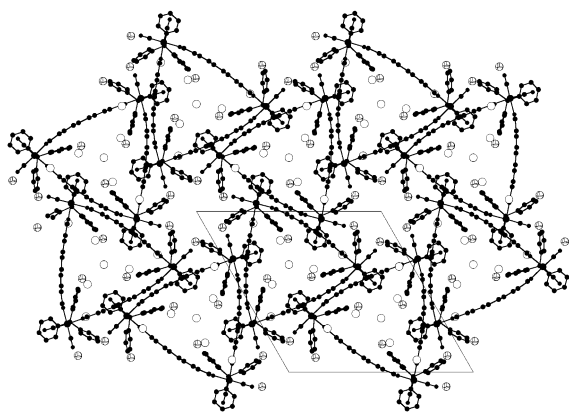


Figure 2. Packed structure of solvated **1** in the solid state along [001] with filled spheres for nonhydrogen atoms of molecule **1**, hollow spheres for CH_2Cl_2 , and octant-shaded spheres for MeOH. The central hollow sphere inside the trigonal channel contains two disordered CH_2Cl_2 molecules at two different depths. All the hydrogen atoms of **1** have been omitted for clarity.

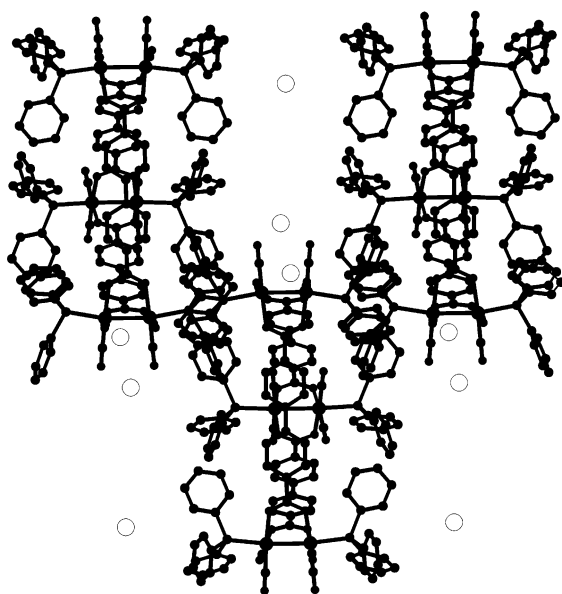


Figure 3. The clefts between two triangular-tube molecules with each cleft containing three CH_2Cl_2 molecules shown as hollow spheres.

the intrinsic 1D trigonal channels (Figure 1), the interstices in **1** also form another 1D “trigonal” channel, which has three MeOH located within, but viewed as a 1D “hexagonal” channel has six hexagonally distributed MeOH molecules in the projection plot (Figure 2). Each hexagonal opening has an edge length of about $13.12(1) \text{ \AA}$. Two separate locations within the trigonal channel were found to accept solvent guests: five CH_2Cl_2 and three MeOH molecules are located inside the triangular tube and three CH_2Cl_2 molecules (each at an average position of two disordered sites) are in the clefts between two triangular tubes and close to the three rims of the molecular triangle (Figure 2 and 3).

After one day, all solvated crystals remain transparent when viewed with an optical microscope. However, after the

crystals were exposed to air at ambient temperature for several hours, the solvent guests evaporated, while the crystals absorbed moisture from the atmosphere. A thermal gravimetric analysis (TGA) of some of these crystals showed a 0.04% weight loss at 81.8°C , which corresponds to the loss of 0.1 H_2O molecules per formula unit. Decomposition of the compound occurred at 203.8°C with another weight loss of 2.46%, which corresponds to the loss of 2.5 CO molecules per formula unit (Figure 4a). The release of water at 81.8°C was

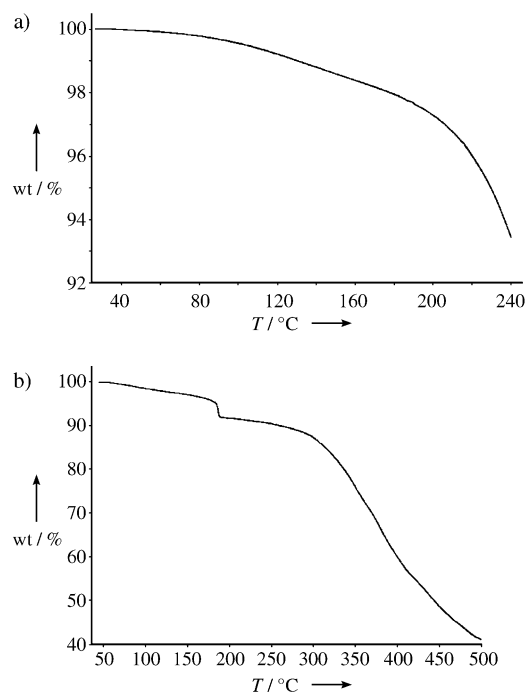


Figure 4. Thermal gravimetric analyses for a) solvated- and b) desolvated-crystals of **1**. Wt = residual weight fraction.

also confirmed by a ^1H NMR study of the product. Interestingly, TGA of some desolvated crystals, obtained after carefully pumping off the solvents, showed that the thermal decomposition occurs at a lower temperature, 181.1°C (Figure 4b). Hence, it is evident that the adsorbed water molecules increase the thermal stability of the molecular framework in **1**.

To understand the framework rigidity and the increased thermal stability of **1** during the drying process, the single-crystal X-ray analysis of an air-dried crystal at 293 K was carried out. Both solvated and air-dried single crystals of **1** maintain an identical space group, $P6_3/m$, but with slightly longer unit-cell lengths and a larger volume ($a=b=23.8883(18)$, $c=20.202(2) \text{ \AA}$, and $V=9984.0(15) \text{ \AA}^3$) in the air-dried crystal relative to the solvated one ($a=b=23.5248(5)$, $c=20.0767(5) \text{ \AA}$, and $V=9622.2(4) \text{ \AA}^3$), probably arising from thermal expansion, which is further supported by the similarity observed in most bond lengths, but not bond angles. Differential scanning calorimetry (DSC) of some typical air-dried crystals showed water desorption, but no apparent phase change up to 175°C . The framework of **1** remains rigid through noncovalent interactions between 150 and 448 K.

From the Fourier difference maps of the air-dried structure **1** (Figure 5), the location of the water molecules in each lattice were assigned on the basis of three residual electron peaks (between 1.1 and 1.3 e Å⁻³).^[5a] Coincidentally, the locations of six water molecules in the air-dried crystal are

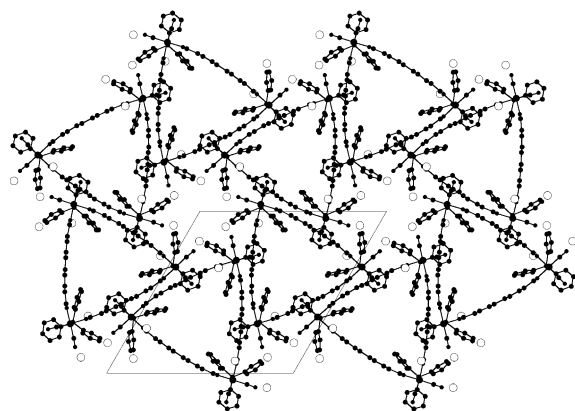


Figure 5. Packing structure of air-dried **1** in the solid state along [001]. All hydrogen atoms are omitted for clarity. Water molecules are shown as hollow spheres.

close to those of MeOH guests in the hexagonal channels of the solvated crystal, and the locations of six other water molecules are also close to those of CH₂Cl₂ guests inside the clefts (compare Figure 2 with Figure 5). It appears that the dipole–dipole attractive interactions between the polar surface of the porous adsorbent, **1**, and the water adsorbates direct site-selective adsorption. However, it is still a physisorption rather than chemisorption, as the closest distances between any water oxygen atom and any other nearby atom, hydrogen or nonhydrogen, are all longer than 3.6 Å. Apparently, the hydrophilic water molecules push the nearby hydrophobic phenyl groups of the phosphane ligands closer together through edge-to-face π – π stacking interactions,^[6] thus increasing both the rigidity and thermal stability of the framework and raising the decomposition temperature from 181.1 °C for the desolvated crystals, to 203.8 °C for the air-dried crystals. The hydrophilic MeOH molecules, used as one of two crystallization solvents for **1**, may also exert similar hydrophobic–hydrophilic interactions, thus facilitating the preorganization of **1**, through intermolecular noncovalent association of phenyl groups of the phosphane ligands, into the porous material. Based on the van der Waals volumes of CH₂Cl₂ and MeOH,^[7] we find that in the solvated **1**, the guest molecules—16 CH₂Cl₂ and 12 MeOH—have a volume of 1.354 Å³, which is 14 % of the unit cell volume. A sorption experiment with an adsorbate, N₂, and **1** as the adsorbent at 77.35 K was also carried out. An apparent BET surface area of 16.12 m² g⁻¹ with a corresponding pore volume of 0.049 cm³ cm⁻³ was obtained.

The results presented herein reveal that a truly molecular zeolite with suitable thermal stability and structural rigidity can be readily synthesized by using tetracarbonyl- and diphosphane-ligated diruthenium as building blocks and dicarboxylates as links. Future investigations will focus on

the synthesis and characterization of similar porous materials with larger pores, elongated triangular tubes, and/or chiral channels by using suitable dicarboxylate links.

Received: February 10, 2003

Revised: April 28, 2003 [Z51149]

Keywords: microporous materials · noncovalent interactions · self-assembly · supramolecular chemistry · zeolite analogues

- [1] I. W. C. E. Arends, R. A. Sheldon, M. Wallau, U. Schuchardt, *Angew. Chem.* **1997**, *109*, 1190; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1144, and references therein.
- [2] a) H. Li, M. Eddaoudi, T. L. Groy, O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 8571; b) H. Li, M. Eddaoudi, M. O’Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276; c) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148; d) C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* **1999**, 375–376; e) K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem.* **2000**, *112*, 4001–4003; *Angew. Chem. Int. Ed.* **2000**, *39*, 3843–3845; f) M. Eddaoudi, H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391; g) B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O’Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 11559–11560; h) M. Kondon, M. Shimamura, S. Noro, S. Minakoshi, A. Asami, K. Seki, S. Kitagawa, *Chem. Mater.* **2000**, *12*, 1288; i) K. Seki, *Chem. Commun.* **2001**, 1496; j) G. Papaefstathiou, L. R. MacGillivray, *Angew. Chem.* **2002**, *114*, 2174–2177; *Angew. Chem. Int. Ed.* **2002**, *41*, 2070–2073.
- [3] G. A. Mines, B.-C. Tzeng, K. J. Stevenson, J. Li, J. T. Hupp, *Angew. Chem.* **2002**, *114*, 162–165; *Angew. Chem. Int. Ed.* **2002**, *41*, 154–157.
- [4] a) A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, New York, **1973**; b) A. Gavezzotti, *Acc. Chem. Res.* **1994**, *27*, 309; c) M. U. Schmidt, U. Englert, *J. Chem. Soc. Dalton Trans.* **1996**, 2077.
- [5] a) See Supporting Information for details of synthesis and characterization, crystal data for solvated and air-dried structures of **1**, and the assignment for the adsorbed water locations in air-dried **1**. b) CCDC-192219 (solvated **1**) and 192221 (air-dried **1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
- [6] J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, Wiley, New York, **2000**, p. 26.
- [7] Y. Marcus, *The Properties of Solvents*, Wiley, New York, **1998**.