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Molecular Tectonics. Three-Dimensional Organic Networks with Zeolitic Properties

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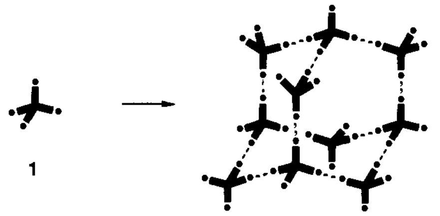
We have defined a *tecton* as a molecule whose interactions are dominated by specific attractive forces that induce the assembly of aggregates with controlled geometries; *molecular tectonics* is then the art and science of supramolecular construction using tectonic subunits.[3] Hypothetical tecton **1** with four tetrahedrally oriented sticky sites (·) is designed to generate diamondoid networks or related three-dimensional lattices (eq 1). For example, intermolecular hydrogen bonding of the tetrahedrally oriented[4] pyridone rings in tecton **2** directs the self-assembly of an interpenetrating diamondoid network that enclathrates guest molecules in large rectangular channels.[3,5,6] We have now demonstrated that the strategy of molecular tectonics can be used to assemble a wide variety of ordered three-dimensional organic networks and that these assemblies have some of the desirable properties of zeolites and related inorganic materials, including high structural integrity, potentially large void volumes, and adjustable microporosity.



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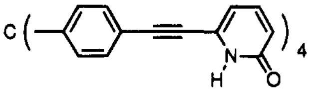

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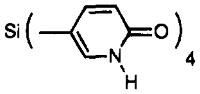

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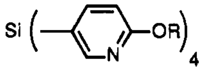
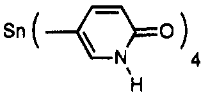


4 (R = CH_2Ph)



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In crystals of clathrate **2**·$2CH_3CH_2CH_2COOH$, the average distance between the tetrahedral centers of adjoining tectons is 19.7(1) Å, the channels are approximately 4 × 8 Å in diameter,[7] and 24% of the total volume is occupied by enclathrated guests.[8,9] To construct contracted diamondoid networks with shorter intertectonic separations, we synthesized tecton **3**. Compound **3** could be prepared conveniently in 52% overall yield from 5-bromo-2-(phenylmethoxy)pyridine[12] by bromine−lithium exchange (BuLi), subsequent addition of $SiCl_4$, and deprotection (CF_3COOH, 25 °C)[13] of the intermediate tetrapyridylsilane **4**.[14] Crystallization of tecton **3** from mixtures of ether and carboxylic acids yielded a series of clathrates of approximate compositions **3**·4 CH_3COOH, **3**·$4CH_3CH_2COOH$, **3**·$CH_3(CH_2)_3COOH$, and **3**·$0.5CH_3(CH_2)_3COOH$·$1CH_3COOH$, and their structures were determined by X-ray crystallography.[15] As expected, clathrate **3**·$4CH_3CH_2COOH$ forms a diamondoid network with an average intertectonic separation of 11.7(1) Å (Figure 1). Despite the shorter separation, the network is perforated by large square channels with diameters of approximately 6 Å,[7,9] which selectively enclose guest molecules of propionic acid. Fully 53% of the volume of the crystals is occupied by guests.[8,9] The guest volume is exceptionally large because the diamondoid network in clathrate **3**·$4CH_3CH_2COOH$ is only doubly interpenetrating, whereas the network defined by clathrate **2**·$2CH_3CH_2CH_2COOH$ is 7-fold interpenetrating.[3]

Diamondoid assemblies built from tectons **2** and **3** cannot withstand an extensive loss of enclathrated guests because the network of hydrogen bonds is not strong enough to resist forces favoring close packing. Nevertheless, the following experiment demonstrates that the networks are porous enough to permit exchange and robust enough to remain intact. Suspending crystals of clathrate **3**·$0.5CH_3(CH_2)_3COOH$·$1CH_3COOH$ in acetic acid/ether (25 °C, 30 min) causes essentially complete internal replacement of valeric acid by acetic acid, as measured by ^1H NMR spectroscopy; moreover, subsequent study by X-ray crystallography shows that *the space group remains the same and the cell dimensions do not change substantially.* Because crystallization of tecton **3** from valeric acid/ether and acetic acid/ether produces clathrates with distinctly different unit cells, this

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(4) Nominally tetrahedral derivatives of tetraphenylmethane and related compounds of group 4 elements typically adopt S_4 molecular symmetry. Csákvári, E.; Shishkov, I. F.; Rozsondai, B.; Hargittai, I. *J. Mol. Struct.* **1990**, *239*, 291.

(5) For related studies of the assembly of organic diamondoid networks directed by hydrogen bonding, see: Ermer, O.; Eling, A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 925. Copp, S. B.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1078. Ermer, O.; Lindenberg, L. *Helv. Chim. Acta* **1991**, *74*, 825.

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(7) The estimated pore sizes correspond to distances between van der Waals surfaces of opposing walls defined by a projection along the channel axis.

(8) Volumes occupied by guests were estimated by using the stoichiometry of the clathrate, its calculated density, and the density of the pure guest at 25 °C.

(9) For comparison, pore sizes in typical zeolites range from approximately 4 to 13 Å, and void volumes are normally less than 50%.[10] The cylindrical channels in urea clathrates are nearly 5 Å in diameter, and the void volumes are approximately 30%.[11]

(10) For references, see: Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756.

(11) Takemoto, K.; Sonoda, N. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 2, p 47. Smith, A. E. *Acta Crystallogr.* **1952**, *5*, 224.

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(14) The structure assigned to this new compound is consistent with its elemental analysis and its IR, ^1H NMR, and ^{13}C NMR spectra. These data are included in the supplementary material.

(15) Crystals of clathrate **3**·$4CH_3COOH$ belong to the monoclinic space group $C2/c$ with $a = 18.744(5)$ Å, $b = 7.870(2)$ Å, $c = 21.703(4)$ Å, $\beta = 101.805(18)°$, $V = 3133.8(13)$ Å^3, $D_{calcd} = 1.366$ g cm^{-3}, and $Z = 4$. Data were collected at 215 K, and the structure was refined to $R_F = 0.039$, $R_w = 0.049$ for 2728 reflections with $I > 1.96\sigma(I)$. Crystals of clathrate **3**·$4CH_3CH_2COOH$ belong to the tetragonal space group $P4_2/n$ with $a = b = 15.645(3)$ Å, $c = 7.6603(17)$ Å, $V = 1875.0(5)$ Å^3, $D_{calcd} = 1.241$ g cm^{-3}, and $Z = 2$. Data were collected at 215 K, and the structure was refined to $R_F = 0.095$, $R_w = 0.090$ for 1182 reflections with $I > 1.96\sigma(I)$. A full description of the structure is provided in the supplementary material. Crystals of clathrate **3**·$CH_3(CH_2)_3COOH$ belong to the orthorhombic space group $Pbcn$ with $a = 23.932(12)$ Å, $b = 21.345(6)$ Å, $c = 11.000(2)$ Å, and $V = 5619(12)$ Å^3. Crystals of clathrate **3**·$0.5CH_3(CH_2)_3COOH$·$1CH_3COOH$ belong to the same space group with $a = 24.538(6)$ Å, $b = 21.337(4)$ Å, $c = 11.002(4)$ Å, and $V = 5760(3)$ Å^3.

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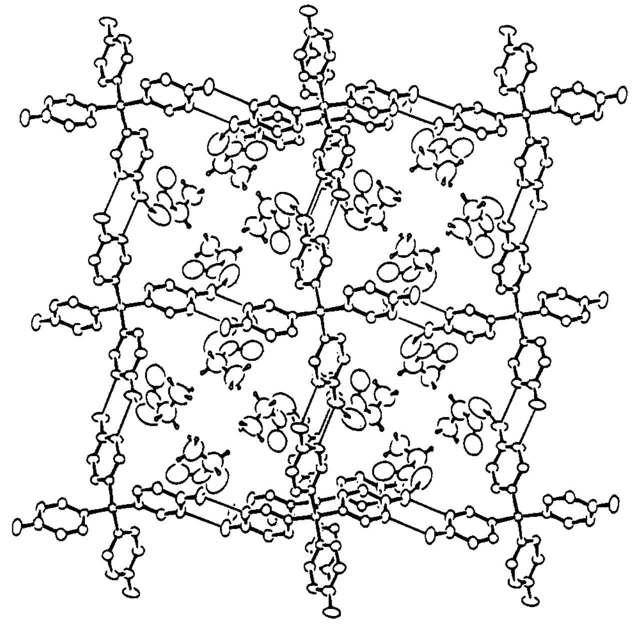

Figure 1. ORTEP drawing of part of the diamondoid network present in crystals of clathrate $\mathbf{3}\cdot4\mathrm{CH_3CH_2COOH}$. The view is parallel to the channel axes and shows the cross sections of four adjacent channels and enclathrated molecules of propionic acid. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability. All hydrogen atoms in tecton **3** are omitted for clarity, while those in propionic acid are shown as spheres of arbitrary size. Hydrogen bonds are represented by narrow lines.

experiment establishes that exchange occurs not by recrystallization, with significant movement of tectonic subunits, but rather by replacement of guests within an intact microporous network.[16]

Diamondoid networks are favored because they accommodate nominally tetrahedral tectons **2** and **3** and permit efficient interpenetration; however, other three-dimensional lattices are also conceivable, particularly when the tecton or its intermolecular interactions are designed to be susceptible to deformations. In a similar way, small variations in the metal−oxygen−metal angles in zeolites allow nominally tetrahedral $\mathrm{SiO_4}$ and $\mathrm{AlO_4}$ units to generate a rich variety of three-dimensional networks.[17] We therefore decided to replace the central atom of silicon in tecton **3** by tin, thereby producing a tecton **5** with a core more susceptible to angular deformations.[18] Tecton **5** was synthesized from 5-iodo-2-pyridone[19] in 33% overall yield by O-silylation (TBDMS-Cl, $\mathrm{N(C_2H_5)_3}$), followed by iodine−lithium exchange (BuLi), addition of $\mathrm{SnCl_4}$, and desilylation ($\mathrm{CH_3COOH}$, 25 °C) of the resulting tetrapyridylstannane. Crystallization of tecton **5** from valeric acid/hexane yielded clathrate $\mathbf{5}\cdot\mathrm{CH_3(CH_2)_3COOH}$, and its structure was determined by X-ray crystallography.[20] Each tecton is linked to four neighbors by direct hydrogen bonding of pyridone rings to create cyclic quartets, which then interlock to build a novel network of parallel four-sided stacks (Figure 2). Each stack has an open diameter of approximately 9 × 2 Å,[6] creating channels selectively filled with well-ordered molecules of valeric acid.[21] Two features permit nominally tetrahedral tecton **5** to form cyclic quartets instead of the cyclic hextets characteristic of diamondoid networks: (1) Two of the four pyridone−pyridone interactions that link tecton **5** into quartets involve only a single hydrogen bond, so the pyridone rings do not need to be coplanar. (2) Bond angles at the central atom of tin in tecton **5** accept substantial deformations. For example, the C−Si−C angles in diamondoid clathrate $\mathbf{3}\cdot4\mathrm{CH_3CH_2COOH}$ range only from 108° to 110°, while the C−Sn−C angles in nondiamondoid clathrate $\mathbf{5}\cdot\mathrm{CH_3(CH_2)_3COOH}$ vary from 102.99(16)° to 119.66(16)°.

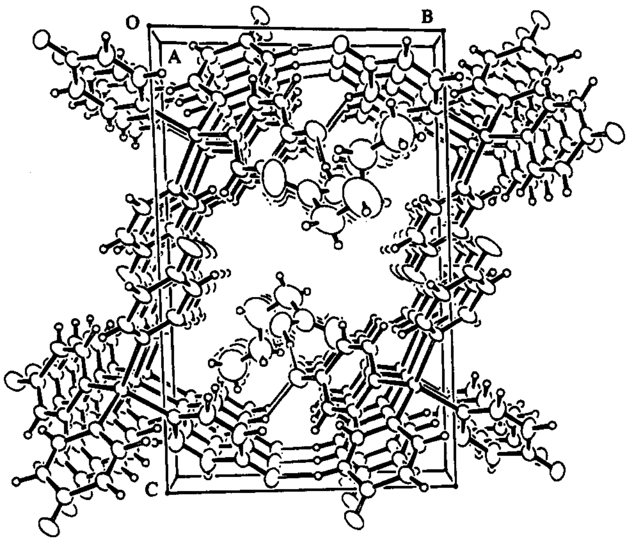

Figure 2. ORTEP view of superimposed unit cells of clathrate $\mathbf{5}\cdot\mathrm{CH_3(CH_2)_3COOH}$ showing a single channel defined by stacked quartets. Pyridones lying in the *ac* plane are doubly hydrogen bonded, while those lying in the *ab* plane are singly hydrogen bonded. Each channel is surrounded by eight parallel channels, all filled with valeric acid. Hydrogen atoms are shown as spheres of arbitrary size, and other atoms are represented by ellipsoids corresponding to 40% probability. Hydrogen bonds are indicated by narrow lines.

These observations are important because they suggest that clever application of the strategy of molecular tectonics can be used to build an unlimited range of ordered three-dimensional organic networks with some of the desirable properties of zeolites and related inorganic materials, including high structural integrity, potentially large void volumes, and adjustable microporosity.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada, the Ministère de l'Éducation du Québec, and the Canada Council for financial support.

Supplementary Material Available: Spectroscopic and analytical data for tectons **3** and **5** and intermediates used in their synthesis and crystallographic data, descriptions of structure determinations, and tables of atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic thermal parameters for clathrates $\mathbf{3}\cdot4\mathrm{CH_3CH_2COOH}$ and $\mathbf{5}\cdot\mathrm{CH_3(CH_2)_3COOH}$ (40 pages); refined and calculated hydrogen atom coordinates for clathrates $\mathbf{3}\cdot4\mathrm{CH_3CH_2COOH}$ and $\mathbf{5}\cdot\mathrm{CH_3(CH_2)_3COOH}$ (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any masthead page for ordering information.

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(16) Classical studies of the exchange of guests in organic clathrates have typically failed to distinguish these alternatives. For example, see: Barrer, R. M.; Shanson, V. H. *J. Chem. Soc., Chem. Commun.* **1976**, 333. For a recent study of slow, partial exchange in urea clathrates, see: Mahdyarfar, A.; Harris, K. D. M. *J. Chem. Soc., Chem. Commun.* **1993**, 51.

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(20) Crystals of clathrate $\mathbf{5}\cdot\mathrm{CH_3(CH_2)_3COOH}$ belong to the triclinic space group $P\bar{1}$ with $a = 8.1803(10)$ Å, $b = 10.485(4)$ Å, $c = 16.173(3)$ Å, $\alpha = 86.199(20)°$, $\beta = 81.510(13)°$, $\gamma = 75.034(20)°$, $V = 1324.9(6)$ Å^3, $D_{\mathrm{calcd}} = 1.497$ g cm^{-3}, and $Z = 2$. Data were collected at 295 K, and the structure was refined to $R_F = 0.038$, $R_w = 0.045$ for 4393 reflections with $I > 3.00\sigma(I)$. A full description of the structure is provided in the supplementary material.

(21) Periodic enlargements of the channels permit the enclathration of valeric acid.