

purge gas. The crystals are thermally stable to above 150 °C after which the TG curve shows a mass loss of about 33 % between 180 and 300 °C, which is consistent with and corresponds to the loss of benzene ($M^+ = 78$) and pyridine ($M^+ = 79$). Further heating leads to decomposition above 400 °C. The IR spectrum shows two strong peaks at 1635 cm^{-1} and 1446 cm^{-1} ; the difference between these peaks is 189 cm^{-1} as would be expected for bridging bidentate carboxylates.^[20]

Crystal data for **1a**: Tetragonal, $P4/ncc$, $a = 19.0356(9)$, $c = 16.253(1)$ Å, $V = 5889.3(6)$ Å³, $Z = 8$ (for $[\text{Zn}_2(1,3\text{-bdc})_2(\text{py})_2]$), $\rho_{\text{calc}} = 1.744$ g cm^{-3} , $\mu = 1.69$ mm⁻¹, $F(000) = 3168$, $2\theta_{\text{max}} = 50.1^\circ$. Crystal data for **1b**: Tetragonal, $P4/ncc$, $a = 18.7912(8)$, $c = 16.8886(10)$ Å, $V = 5963.5(8)$ Å³, $Z = 8$ (for $[\text{Cu}_2(1,3\text{-bdc})_2(\text{py})_2]$), $\rho_{\text{calc}} = 1.507$ g cm^{-3} , $\mu = 1.48$ mm⁻¹, $F(000) = 2750$, $2\theta_{\text{max}} = 56.54^\circ$. The data for **1a** and **1b** were collected at -100 °C on a Bruker SMART APEX diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) and were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 .^[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the pyridine and bdc ligands were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their parent atoms. The guest molecules inside the bowl-shaped cavity were disordered in such a manner that they could not be readily resolved. Guest molecules in the hour-glass-shaped channels were better resolved, but it is not possible to differentiate between benzene and pyridine molecules in these channels. Guest atoms were therefore treated as carbon atoms and refined with fixed isotropic thermal parameters and variable site occupancy. Final residuals for **1a** were $R1 = 0.0372$ and $wR2 = 0.0958$ for 1782 reflections with $I > 2\sigma(I)$, and $R1 = 0.0591$, $wR2 = 0.1028$ for all 2625 data (181 parameters). Values for **1b** were $R1 = 0.0407$ and $wR2 = 0.1063$ for 2289 reflections with $I > 2\sigma(I)$, and $R1 = 0.0680$, $wR2 = 0.1139$ for all 3632 data. Residual electron density was 0.82 and -0.58 e Å⁻³ for **1a** and 0.96 and -0.87 e Å⁻³ for **1b**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152547 and CCDC-162957. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: November 27, 2000

Revised: March 19, 2001 [Z 16185]

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Polygons and Faceted Polyhedra and Nanoporous Networks**

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Design principles that are based upon the concepts of crystal engineering and self-assembly have recently afforded new classes of crystalline solids that possess important physical properties such as bulk magnetism^[1, 2] or porosity.^[3–5] Furthermore, given that these structures are designed from first principles, they offer chemists an inherent ability to control the chemical nature of the molecular components and therefore influence the bulk physical properties of the material. Similar principles of self-assembly have been applied toward the design and isolation of nanosized spheroid architectures that are based upon regular (Platonic) and semiregular (Archimedean) polyhedral solids.^[6–13] However, there exist other well-documented examples of uniform polyhedra^[14, 15] that to our knowledge remain unexplored at the molecular level. In particular, there are nine polyhedra that are closely related to Platonic and Archimedean solids but differ in that they can be designed and built through linking of the vertices of polygons rather than the edges of polygons. Such structures are termed *faceted polyhedra*^[16] (Figure 1a) since they necessarily contain both open and closed faces. Of particular interest in the context of this study are those polyhedra that are sustained by triangles, squares, or combinations thereof.

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[**] M.J.Z. gratefully acknowledges the financial support of the NSF (DMR 0101641).

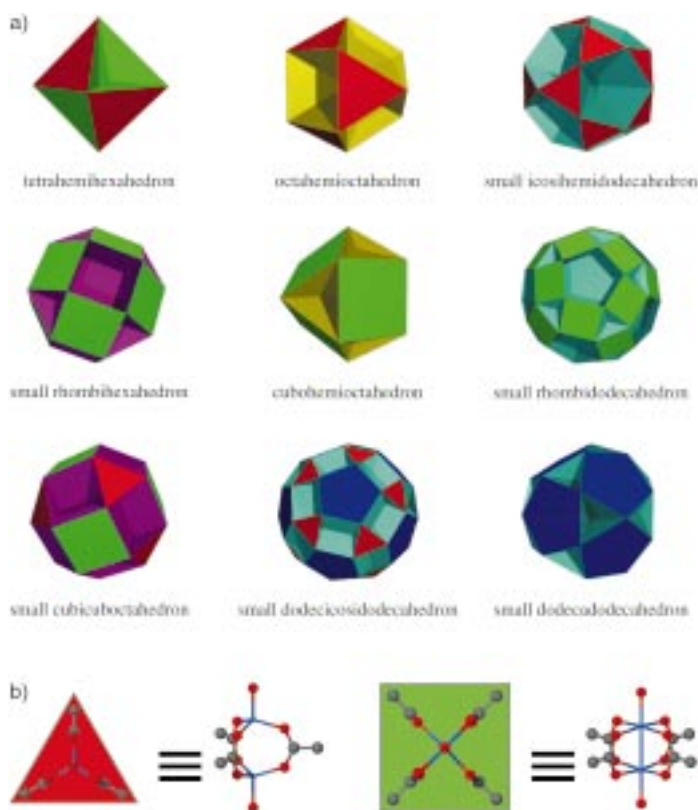


Figure 1. a) Schematic illustrations of the nine possible faceted polyhedra; throughout this contribution squares are color-coded green and triangles red. b) The secondary building units (SBUs) employed for the construction of faceted polyhedra in this study.

The molecular triangles and squares that we have targeted for study are the previously reported metal-organic secondary building units^[17] (SBUs) $M_2(RCO_2)_3$ (**A**) and $M_2(RCO_2)_4$ (**B**) (Figure 1b). It has already been demonstrated that use of polycarboxylate ligands in $M_2(RCO_2)_4$ (e.g. benzene-1,4-dicarboxylate) affords self-assembled infinite structures with predictable topology and relatively high thermal stability.^[18] It therefore occurred to us that complexation of the angular trifunctional ligand benzene-1,3,5-tricarboxylate (btc) with **A** and **B** should also afford predictable infinite networks. Indeed, complexation of btc with Zn^{II} affords two remarkable new structures that represent prototypes for porous structures that are based upon faceted uniform polyhedra.

Small cubicuboctahedra (1): The crystal structure of **1** (Figure 2) can be described as being composed of molecular squares (green) and triangles (red) that self-assemble into small cubicuboctahedra because two of the btc carboxylate moieties impose a 120° angle at the linkage between the polygons. There are eight triangular faces and six square faces and each square face is fused (i.e. shared) with the square face of an adjacent small cubicuboctahedron. The framework portion of **1** should therefore be formulated $\{[Zn_2(btc)]_8[Zn_2(btc)_{1.333}]_3\}_n$ or $(A_8B_3)_n$. The connectivity of the small cubicuboctahedra generates one of the other faceted polyhedra, an octahemiocuboctahedron (see Figure 1a). The framework exhibited is low density because the faceted polyhedra are inherently open (white squares and channels in schematic portion of Figure 2).

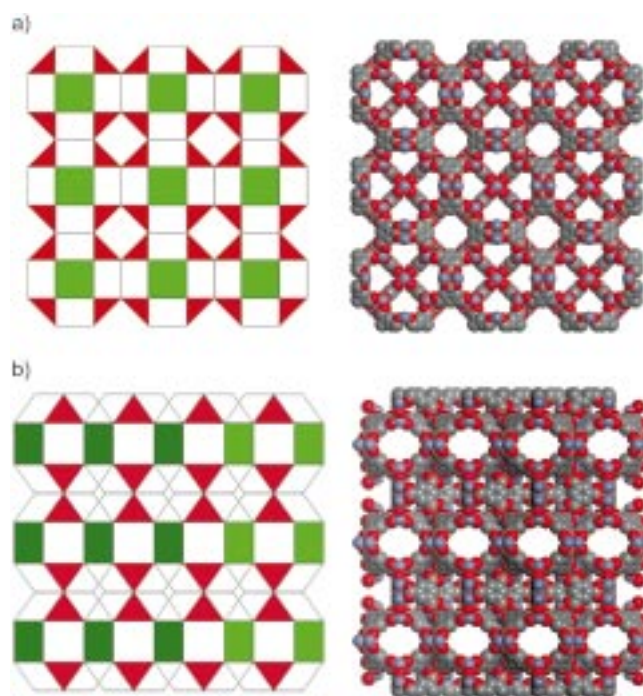


Figure 2. Crystal structure and schematic illustration of $\{[L_2Zn_2(btc)_1]_8[L_2XZn_2(btc)_{1.333}]_3\}_n$ (**1**; L = pyridine or water, X = NO_3^-). a) View along the [100] crystallographic plane and b) view along the [110] crystallographic plane. The schematics illustrate how these structures are generated by close packing and predict the openness of the observed crystal structure of **1**.

An aspect of uniform polyhedra that makes them desirable as nanoscale building blocks is that there is inherently a great deal of control concerning the framework geometries that they must adapt if they close-pack (tessellate). For example, for combinations of Platonic and Archimedean polyhedra, there exist only eleven possible space-filling infinite frameworks. However, there are even greater restrictions for faceted polyhedra since they must pack such that each polygon is connected only by its vertices and does not share its edges. Indeed, the possible close-packing modes for faceted polyhedra are restricted to only three related space-filling architectures (Figure 3a; see also Figure 1a): rhombicuboctahedra/cuboctahedra/cubes (1:1:3); rhombicuboctahedra/cubes/tetrahedra (1:1:2); cuboctahedra/octahedra (1:1). These structures have long-been documented^[19, 20] and correspond to self-assembly of triangles and squares or squares only. Indeed, Andreini^[21] and Wells^[22] have already discussed these networks in terms of the space group symmetry of the network edge-skeletons.

Since the small cubicuboctahedron in **1** has a congruent edge-skeleton with a rhombicuboctahedron (Figure 3b), it must adapt one of only two possible frameworks. Furthermore, only one of these frameworks can sustain vertex-only connected triangles and squares. It therefore follows that self-assembly of small cubicuboctahedra can result in only one framework, 3a. The structure of **1** therefore appears to be preordained and, furthermore, is clearly prototypal for other frameworks that might be formed from other molecular triangles and squares. The dimensions of the small cubicuboctahedron in **1** are the same as the unit cell dimensions, as

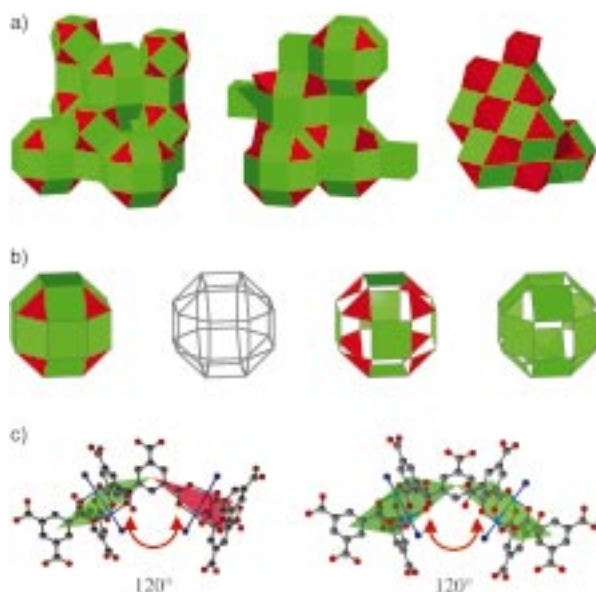


Figure 3. a) Schematic illustrations of the three uniform space fillings based upon Platonic and Archimedean polyhedra that are possible for faceted polyhedra. b) A schematic illustration of how the small cubicuboctahedron and the small rhombihexahedron have a congruent edge-skeleton with the rhombicuboctahedron. c) An illustration of how the vertices of the molecular squares and triangles are connected by the btc moieties.

there is only one small cubicuboctahedron per unit cell. The separation between opposite square faces is therefore 2.05 nm and the dimensions of the windows are about 0.9 nm. The overall structure contains channels and cavities that are entirely predictable based upon the dimensions of **A**, **B**, and btc. Notably, the dihedral angle imposed by the btc ligands (120°) is close to the ideal angle of $125^\circ 16'$ that would exist in a perfect small cubicuboctahedron (Figure 3c).

Small rhombihexahedra (2): The crystal structure of **2** (Figure 4) consists of small rhombihexahedra, which also have congruent edge-skeletons with the rhombicuboctahedron (Figure 3b) that are fused at the square faces. Once again, there is only one possible space-filling arrangement that generates a close-packed framework for these polyhedra, a structure that must be based upon squares alone, dihedral angles of 120° (Figure 3c), and the rhombicuboctahedron edge-skeleton: rhombicuboctahedra/cubes/tetrahedra (1:1:2), 4b. The small rhombihexahedron in **2** is slightly larger than the polyhedron seen in **1**. It has a diameter of 2.30 nm and the triangular windows have dimensions of about 0.9 nm. An isostructural analogue of **2** was recently reported by Williams et al., $[\text{L}_3\text{Cu}_3(\text{btc})_2]_n$, $\text{L} = \text{pyridine}$.^[23]

Single crystals of **1** and **2** are stable indefinitely when in contact with mother liquor. Weight losses of 7.2 and 8.2%, respectively, consistent with loss of methanol occur under ambient conditions (isothermal room-temperature thermogravimetric analysis (TGA)), and the samples remain crystalline as confirmed by single-crystal diffraction patterns that are consistent with the frameworks of **1** and **2**. Greater weight losses and irreversible decomposition occur upon heating and correspond to further loss of methanol and then loss of coordinated pyridine molecules (confirmed by TG-MS). The interconnectivity of the cavities in **1** and **2** is quite different

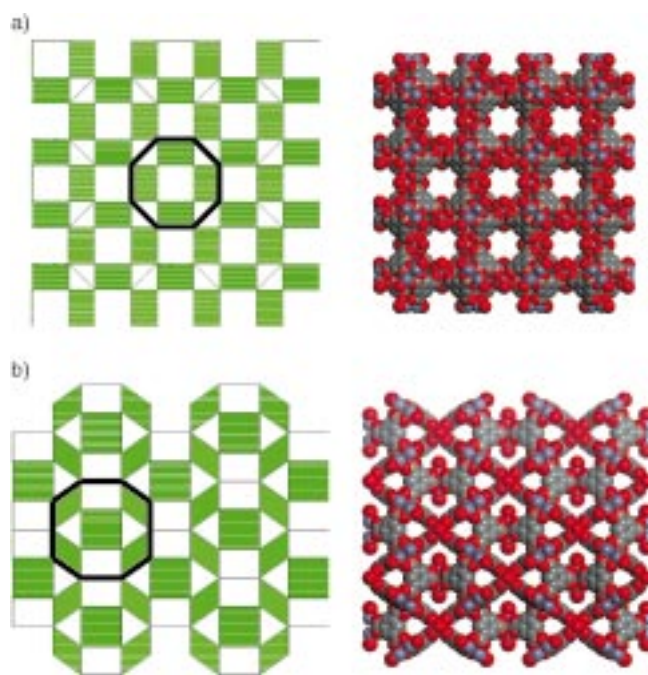


Figure 4. Crystal structure and schematic illustration of $[\text{L}_2\text{Zn}_2(\text{btc})_{1.333}]_{12n}$, (**2**; $\text{L} = \text{pyridine}$ or water). a) View along the [100] crystallographic plane and b) view along the [110] crystallographic plane. Note how the schematics predict the porosity observed in the crystal structure of **2**.

but the windows (0.9 nm) and free volume of the desolvated structures (calculated using Cerius² to be about 75.6 and 70.3% for **1** and **2**, respectively) are similar.

In summary, we have demonstrated that molecular polygons can self-assemble at their vertices to produce molecular architectures and crystal structures that are consistent with long-established geometric constraints. These structures therefore differ in terms of design and function from structures that are generated from Platonic and/or Archimedean building blocks. The strategy represents a potentially broad-ranging approach to the design of nanoporous structures from a wide range of chemical components that are based upon molecular shape rather than chemical formula. In effect, we present another example of the “Molecular Meccano”^[24] approach to self-assembled structures.

Experimental Section

1: A solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (220 mg, 0.741 mmol) and 1,3,5-benzenetricarboxylic acid (220 mg, 1.05 mmol) in methanol (10 mL) was layered onto a solution of nitrobenzene (10 mL) containing pyridine (0.23 mL, 2.8 mmol). Large single crystals ($0.30 \times 0.30 \times 0.15$ mm) formed within hours under ambient conditions. Crystal data of **1**: $[\text{L}_2\text{Zn}_2(\text{btc})]_8[\text{XL}_2\text{Zn}_2(\text{btc})_{1.333}]_3$ ($\text{L} = \text{C}_5\text{H}_5\text{N}$ or H_2O , $\text{X} = \text{NO}_3^-$), $M_r = 5018.1$, cubic, $Pm\bar{3}m$, $a = b = c = 20.4582(13)$ Å, $V = 8562.5(9)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 0.973$ g cm⁻³, $2\theta_{\text{max}} = 37.7^\circ$ ($-18 \leq h \leq 15$, $-6 \leq k \leq 18$, $-18 \leq l \leq 18$), $T = 173$ K, 14454 measured reflections, $RI = 0.1278$ for 510 reflections ($I > 2\sigma(I)$), $wR2 = 0.3648$ for 740 independent reflections (all data) and 104 parameters, $GOF = 1.559$.

2: A solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (202 mg, 0.679 mmol) and 1,3,5-benzenetricarboxylic acid (126 mg, 0.600 mmol) in methanol (10 mL) was layered onto a solution of benzene (10 mL) containing pyridine (0.10 mL; 1.24 mmol). Large single crystals ($0.30 \times 0.25 \times 0.20$ mm) formed within hours under ambient conditions. Crystal data of **2**: $[\text{L}_2\text{Zn}_2(\text{btc})_{1.333}]_{12n}$ ($\text{L} =$

C_3H_5N or H_2O), $M_r = 7084.54$, cubic, $Fm\bar{3}m$, $a = b = c = 26.5200(13)$ Å, $V = 18651.8(16)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.261$ g cm⁻³, $2\theta_{\text{max}} = 50.0^\circ$ ($-31 \leq h \leq 31$, $-31 \leq k \leq 18$, $-28 \leq l \leq 31$), $T = 173$ K, 22842 measured reflections, $RI = 0.0602$ for 670 reflections ($I > 2\sigma(I)$), $wR2 = 0.1840$ for 891 independent reflections (all data) and 63 parameters, $GOF = 0.990$.

Data were collected on a Bruker SMART-APEX CCD diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), operating in the Ω and φ scan mode. All crystal data were corrected for Lorentz and polarization effects, and the SADABS^[25] program was used for absorption correction. The structures were solved by direct methods and the structure solutions and refinements were based on $|F^2|$. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were placed in calculated positions and given isotropic U values 20% higher than the atom to which they are bonded. All crystallographic calculations were conducted with the SHELXTL^[26] software suite. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-156776 (1) and CCDC-156777 (2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: January 25, 2001 [Z16502]

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A Rationally Designed NH_4^+ Receptor Based on Cation– π Interaction and Hydrogen Bonding**

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Design and synthesis of ammonium ion receptors have received much attention, not only because ammonium binding is one of the fundamental problems of molecular recognition, but also because such receptors serve as an essential component of sensors used in clinical^[1] and environmental analyses.^[2] Most of the NH_4^+ receptors known to date harness hydrogen bonding in binding an ammonium ion.^[3] For example, nonactin (see Scheme 1), a natural antibiotic agent and one of the most effective NH_4^+ receptors, utilizes four ethereal and four carbonyl oxygen atoms to bind NH_4^+ through hydrogen bonding.^[4] While hydrogen bonding is most commonly involved in molecular recognition, cation– π interaction has drawn much attention in recent years.^[5] In fact, cation– π interaction has been successfully employed in designing synthetic receptors for alkylammonium ions and alkali metal ions.^[5, 6] Despite extensive theoretical studies on NH_4^+ – π interaction, however, no synthetic NH_4^+ receptor exploiting cation– π interaction had been reported until recently. We recently reported a novel NH_4^+ receptor based on tris(pyrazol-1-ylmethyl)benzene that is highly selective for binding NH_4^+ over alkali metal ions.^[7] Subsequent theoretical studies on this receptor by us^[8] and others^[9] suggest that the cation– π interaction between the substrate and the central benzene ring of the receptor plays a significant role in the binding affinity and selectivity of the tripodal receptor toward NH_4^+ . Despite the high selectivity, however, the ion-selective electrode (ISE) based on this receptor shows low sensitivity and strong pH dependence of its performance in comparison to a nonactin-based ISE, and this hampers practical applications as a sensor. Here we present a rationally designed cage-type NH_4^+ receptor that binds the cation by both cation– π interaction and hydrogen bonding, with high sensitivity and selectivity comparable or superior to those of nonactin over a wide range of pH.

In designing the receptor, we considered the following stereoelectronic features: 1) spatial distribution of lone-pair

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[**] We gratefully acknowledge the Korean Ministry of Science and Technology (Creative Research Initiative Program) for support of this work, and the Korean Ministry of Education (Brain Korea 21 program) for graduate studentships to J.H. and W.S.J. M.K. is grateful to POSTECH for an Undergraduate Research Fellowship. We also thank Professor P. K. Bharadwaj for helpful discussions.

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