

## SECTION 4: SUPRAMOLECULAR CRYSTALS

Cavity-Containing Materials Based Upon Resorcin[4]arenes  
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Strategies for the design of multimolecular hosts that display recognition properties analogous to those of monomolecular predecessors are described. In particular, the bowl-shaped cavity of a molecular receptor known as resorcin[4]arene has been elaborated, using hydrogen bonds, for the construction of open and closed cavities that accommodate single and multiple guest species. Both chemical and geometric considerations derived from these studies have led us to identify host frameworks, based upon the five Platonic and 13 Archimedean solids, which have yet to be synthesized or discovered and we propose such systems as targets in chemical synthesis. © 2000 Academic Press

**Key Words:** host-guest chemistry; hydrogen bonds; resorcin[4]arenes; crystal engineering.

## INTRODUCTION

Chemistry has witnessed the emergence of an approach to chemical synthesis that focuses on the exploitation of non-covalent forces (e.g., hydrogen bonds,  $\pi$ - $\pi$  interactions) for the design of multicomponent supramolecular frameworks (1). Fascination with nature's ability to direct the self-assembly of small subunits into large superstructures (e.g., viruses, fullerenes), coupled with a desire to construct materials possessing unique bulk physical properties (e.g., optical, magnetic), has undoubtedly provided a major impetus for their design (2).

*Multicomponent Hosts*

Along these lines, there is much interest in utilizing non-covalent forces, particularly in the form of hydrogen bonds, for the construction of multicomponent hosts (e.g., molecular capsules **1**) that display recognition properties analogous to their monomolecular predecessors (e.g., carcerands **2**) (3, 4). Such cavity-containing frameworks typically involve replacing covalent bonds with supramolecular synthons

that retain the structural integrity of the parent host molecule (Scheme 1).

Notably, in addition to providing access to systems which are difficult to obtain using conventional covalent approaches to molecular synthesis (5), such frameworks can display properties not found in the molecular analog (e.g., reversible formation), which, in some instances, can bear relevance in understanding related biological phenomena (e.g., virus formation) (6).

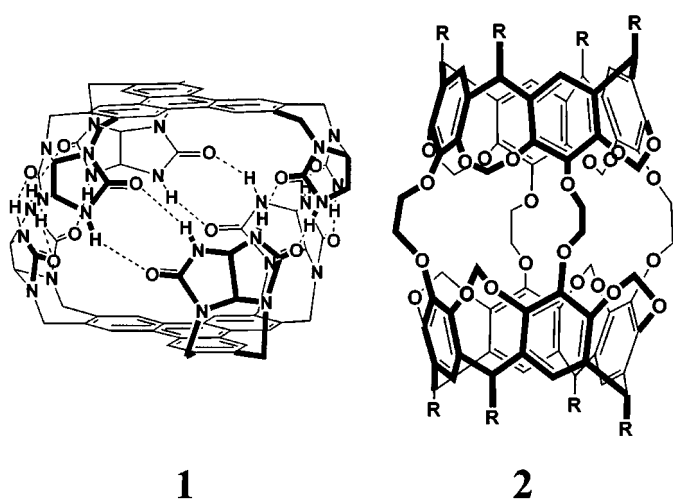
*Resorcin[4]arenes for Multicomponent Host Design*

With this in mind, we recently initiated a program of study aimed at extending the cavities of resorcin[4]arenes supramolecularly (7). As a starting point, we chose the readily available *C*-methylcalix[4]resorcinarene **3** (R = Me) as a platform for the assembly process (8). Indeed, solid state studies revealed the ability of **3** to adopt a bowl-like conformation with  $C_{2v}$  symmetry in which four upper rim hydroxyl hydrogen atoms of **3** are pointed upward above the cavity of the macrocycle which, in turn, effectively make **3** a quadruple hydrogen bond donor (9) (Scheme 2).

*Elaborating resorcin[4]arenes supramolecularly.* Using a resorcinol-based supramolecular synthon (10) **4** for host design, we reasoned that cocrystallization of **3** with hydrogen bond acceptors such as pyridines would result in formation of four O-H...N hydrogen bonds between the upper rim of **3** and four pyridine units which would, in turn, extend the cavity of **3** and yield a discrete, multicomponent host, **3**·4(pyridine) **5** (where pyridine = pyridine and derivatives), capable of entrapping a guest, **3**·4(pyridine)·guest. Furthermore, in addition to a discrete system, we reasoned that by using a linear *exobidentate* molecular spacer unit such as 4,4'-bipyridine, it should be possible to link together **3** in the solid state for the formation of an extended, one-dimensional (1D) array, **3**·2(4,4'-bipyridine)·guest **6** (7).

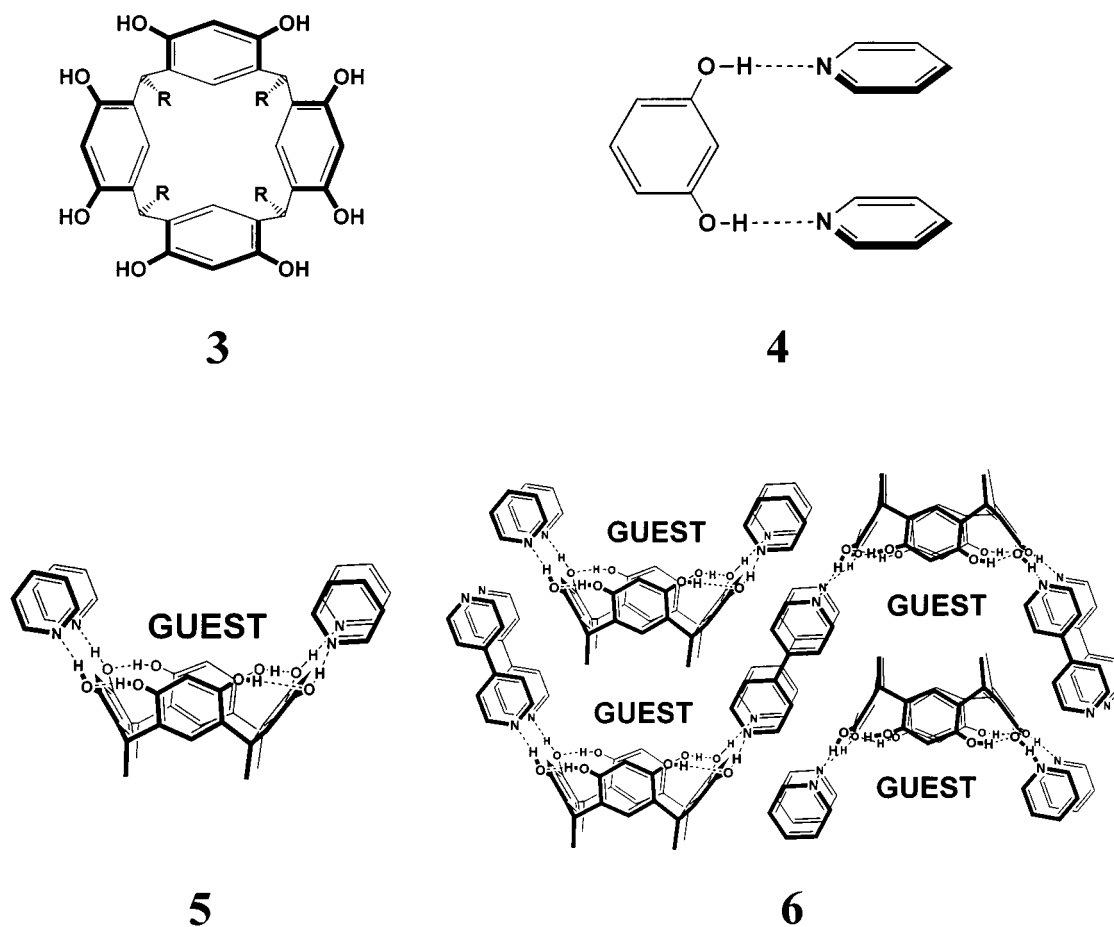
*A spherical container assembly.* During these studies, we also discovered the ability of **3** to self-assemble in solution

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SCHEME 1

and the solid state as a spherical hexamer, along with eight water molecules, to form, in a similar way to **1**, a spherical container assembly held together by 60 O-H...O hydrogen bonds **7** (Fig. 1a) (11).



SCHEME 2

The assembly, which is chiral, was found to possess a well-defined central cavity with a maximum diameter of 1.8 nm and an internal volume of about 1.4 nm<sup>3</sup>, a volume five times larger than the largest molecular capsule previously reported (12). Notably, consultation of polyhedron models revealed the structure of **7** to conform to a snub cube, one of the 13 Archimedean solids (Fig. 1b) (13). Indeed, from these observations we concluded that to design related spherical containers, one must consider the limited topologies available in space for such frameworks (i.e., the 5 Platonic and 13 Archimedean solids) (11).

### DEEP CAVITIES

Previous work toward elaborating the cavity of either a resorcin[4]arene or a calix[4]arene has focused upon the incorporation of substituents along the wider rim of the macrocycle via the formation and breakage of covalent bonds (7). Such an approach to synthesis, however, can often be tedious and time consuming in which the product, which is typically obtained in low yield, may not exhibit a desired property (4). A supramolecular approach to the problem of deepening the cavity of a bowl-shaped macro-

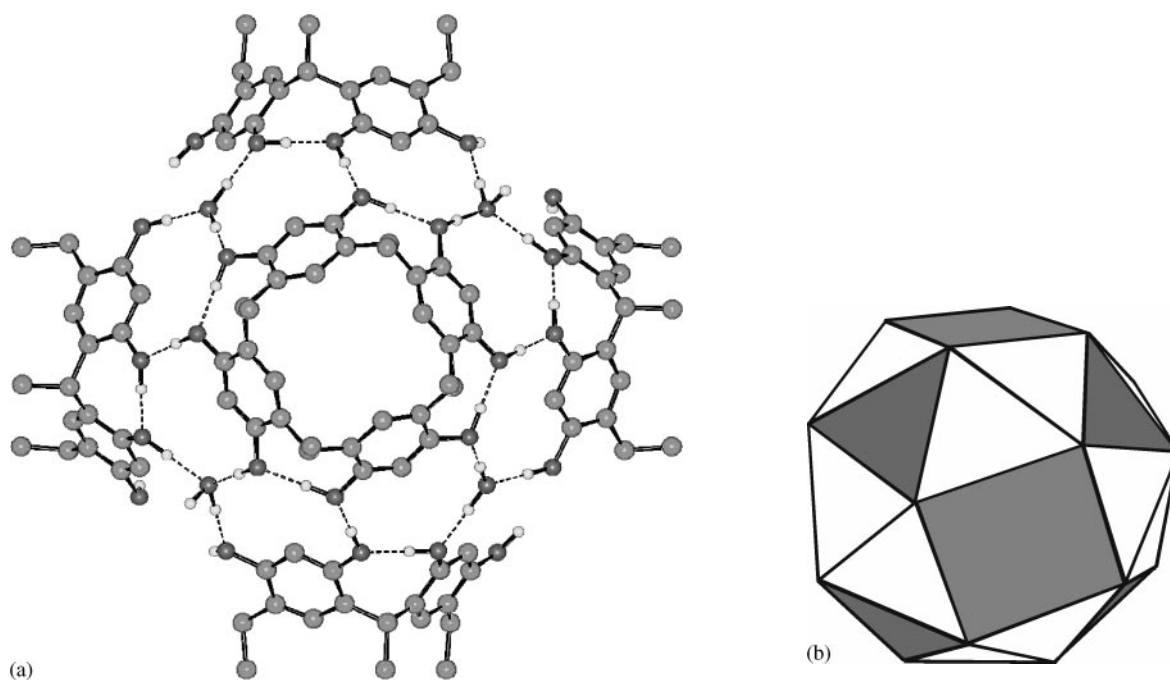


FIG. 1. (a) Cross-sectional view of the X-ray crystal structure of **7** and (b) snub cube.

cycle, however, can, in principle, circumvent the disadvantages of employing a covalent methodology. By using appropriately functionalized molecular components, a deep-cavity host framework, based upon a parent molecule, can be rapidly generated in virtually quantitative yield.

#### Discrete Cavities

For the design of a discrete, multicomponent cavity based upon **3**, we turned to monopyridines. Indeed, we anticipated

the nitrogen atoms of such aromatic systems, upon assembling with **3**, to participate in single O–H⋯N hydrogen bonds along the upper rim of the macrocycle.

*Cavities based upon rigid extenders.* The product of the cocrystallization of **3** with pyridine, from boiling pyridine, is shown in Fig. 2 (7). The assembly is bisected by a crystallographic mirror plane and consists of **3** and five molecules of pyridine, four of which form four O–H⋯N hydrogen bonds, as two face-to-face dimers, such that they adopt an

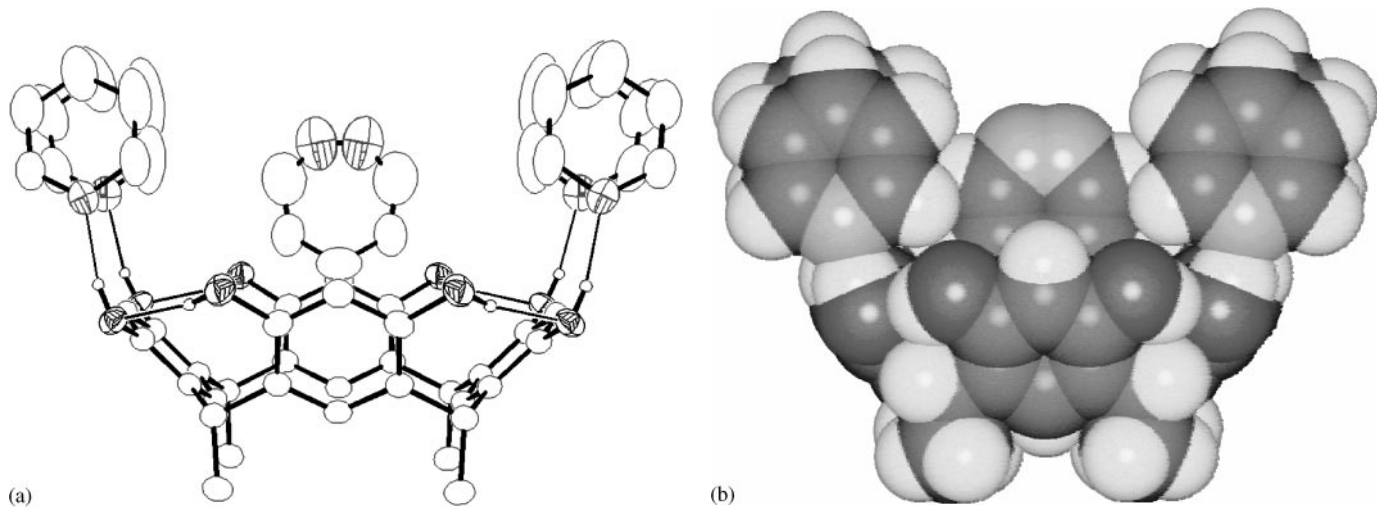
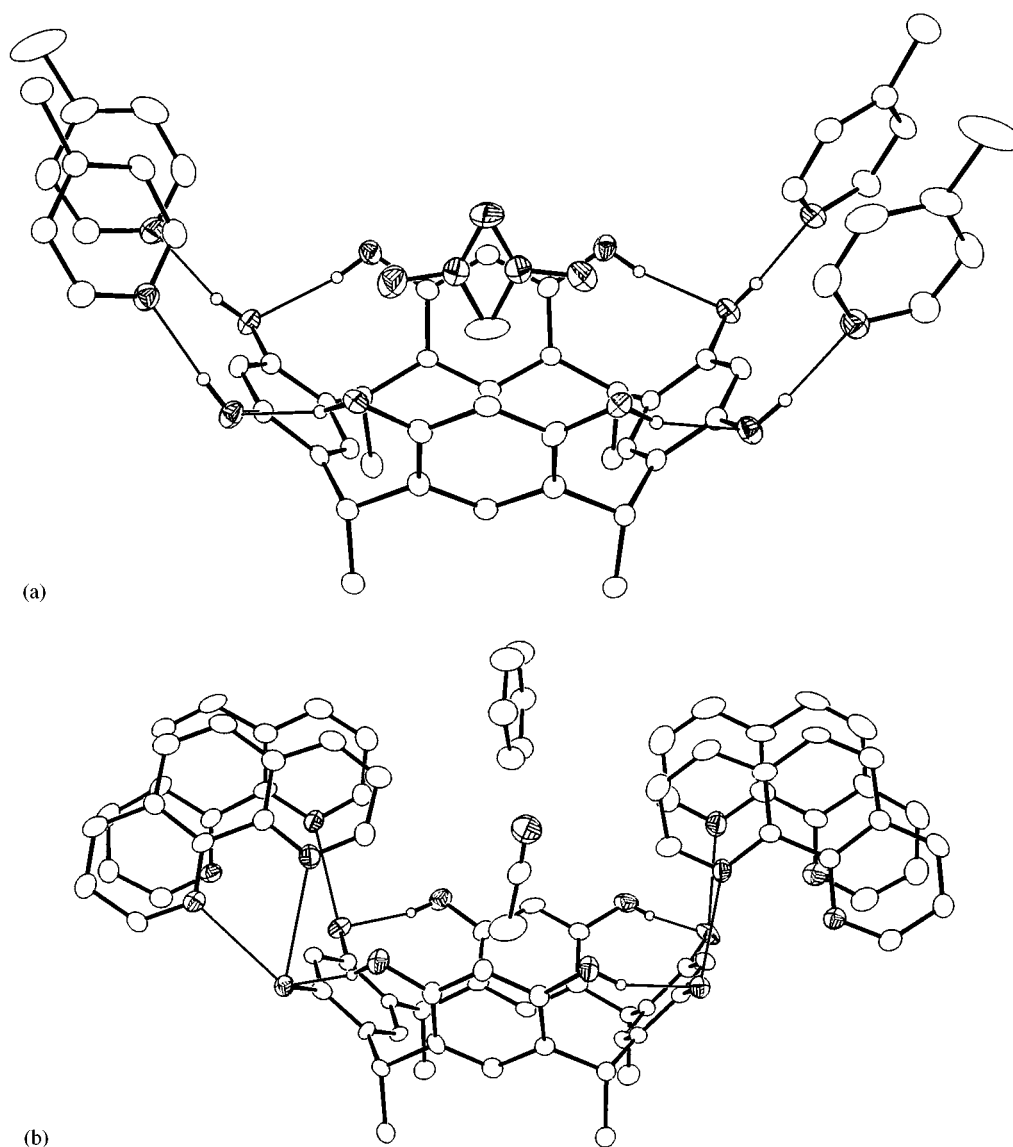


FIG. 2. X-ray crystal structure of **3**·4(pyridine)·pyridine: (a) ORTEP perspective and (b) space-filling view. The pyridine molecule located within the cavity lies disordered across a crystallographic mirror plane.

orthogonal orientation, in a similar way to **4**, with respect to the upper rim of **3**. As a consequence of the assembly process, a cavity has formed inside which a disordered molecule of pyridine is located, interacting with **3** by way of C-H... $\pi$ -arene interactions (14). The remaining hydroxyl hydrogen atoms of the six-component assembly form four intramolecular O-H...O hydrogen bonds along the upper rim of **3**, resulting in a total of eight structure-determining O-H... $X$  ( $X = \text{N}, \text{O}$ ) forces. Indeed, the inclusion of an aromatic such as pyridine within **3**·4(pyridine) is reminiscent of the ability of covalently modified calix[4]arenes, such as *p*-*tert*-butylcalix[4]arene, to form molecular complexes with aromatics such as benzene and toluene (15).

To determine whether it is possible to isolate a guest within **5** which, unlike **3**·4(pyridine), is chemically different than the "substituents" hydrogen bonded to the upper rim of **3**, we next turned to pyridine derivatives, namely, 4-picoline (monopyridine) and 1,10-phenanthroline (bipyridine) (16). In a similar way to pyridine, both molecules possess hydrogen bond acceptors along their surfaces and  $\pi$ -rich exteriors which we anticipated would allow these components to assemble along the upper rim of **3** as stacked dimers. As shown in Fig. 3, cocrystallization of **3** with either 4-picoline or 1,10-phenanthroline from MeNO<sub>2</sub> and MeCN, respectively, yielded six-component complexes, **3**·4(4-picoline)·MeNO<sub>2</sub> and **3**·4(1,10-phenanthroline)·



**FIG. 3.** ORTEP perspective of: (a) **3**·4(4-picoline)·MeNO<sub>2</sub> and (b) **3**·4(1,10-phenanthroline)·MeCN. The included MeNO<sub>2</sub> molecules lies disordered on a crystallographic twofold rotation axis.

MeCN, which are topologically equivalent to the parent pyridine system (7). Unlike the parent assembly, however, the cavities created by the five molecules were occupied by guests chemically different than the walls of the host. Indeed, this observation illustrated that this approach to discrete, deep-cavity frameworks based upon **3** is not limited to two different components. Notably, whereas the 4-picoline moiety was observed to interact with **3** by way of conventional O–H...N hydrogen bonds, the 1,10-phenanthroline extender was, in addition to a conventional hydrogen bond, observed to interact with **3** by way of a three-center, bifurcated O–H...N interaction.

*A cavity based upon a flexible extender.* With the realization that **5** may be exploited for the inclusion of guests different than the supramolecular extenders of **3** achieved, we shifted our focus to pyridines that possess flexible substituents. In addition to introducing issues of stereochemistry, we anticipated that this approach would allow us to further address the robustness and structural parameters which define **4** and thereby aide the future design of analogous host–guest systems based upon **3**.

Our first study in this context has involved 4-vinylpyridine (17). As shown in Fig. 4, in a similar way to the discrete systems described above, four 4-vinylpyridines assemble along the upper rim of **3**, as two face-to-face stacked dimers, in **3**·4(4-vinyl-pyridine)·MeNO<sub>2</sub>, to form a six-component assembly. Interestingly, the olefins of this system, in contrast to resorcinol·4-vinylpyridine (Fig. 4b), adopt a parallel orientation in the solid state, the bonds being separated by a distance of 4.18 Å. Notably, approaches that utilize supramolecular host frameworks to promote alignment of olefins in the solid state, for conducting [2 + 2] photochemical reactions, for example, are rare

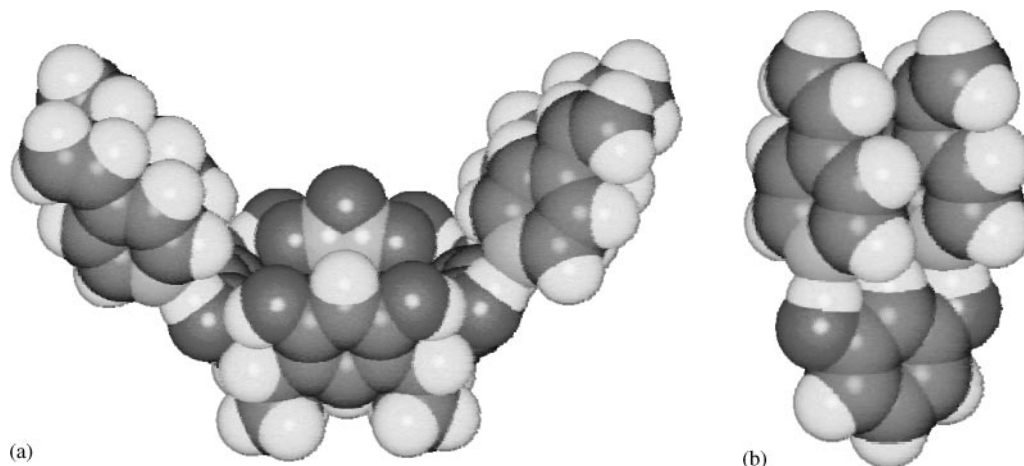
(18) and these observations suggest that similar complexes based upon **3** may provide a route to achieving this goal.

### Infinite Systems

An attractive feature of this design strategy lies in its modularity. In addition to permitting the design of discrete multicomponent frameworks, it is possible, in principle, to link together molecules of **3**, in the bowl conformation, to give rise to infinite assemblies. Owing to the molecular recognition properties of **3**, such materials would be expected to display inclusion properties based upon the ability of **3** to selectively include guests within the cavity of the host.

*Inclusion of single guests.* As shown in Fig. 5, cocrystallization of **3** with 4,4'-bipyridine from MeCN yielded **3**·2(4,4'-bipyridine)·MeCN in which four O–H...N hydrogen bonds form between four hydroxyl groups of **3** and two stacked pyridines (7). Owing to the ability of 4,4'-bipyridine, and its stacked dimer, to serve as a linear bifunctional hydrogen bond acceptor, the components were observed to assemble such that they form a 1D wave-like polymer **6** in which the MeCN solvent molecule is located within the cavity of **3**. That this 1D assembly may be exploited to host a different guest (e.g., MeNO<sub>2</sub>, Me<sub>2</sub>CO), as well as be produced using a different linear bridging unit (e.g., 4,4'-dipyridyl butanedioate), was also realized (19). Thermal studies of these host–guest materials also revealed that the stability of the 1D framework is, in general, independent of the nature of the guest, the guest dissociating from the solid at approximately 190°C (19).

*Inclusion of multiple guests.* In an effort to further develop the host-guest chemistry of **6**, the ability of **6** to include two guests, which assemble as a van der Waals type complex



**FIG. 4.** Space-filling view of the X-ray crystal structure of (a) **3**·4(4-vinylpyridine)·MeNO<sub>2</sub> and (b) resorcinol·2(4-vinylpyridine). The included MeNO<sub>2</sub> molecule lies disordered on a crystallographic twofold rotation axis.

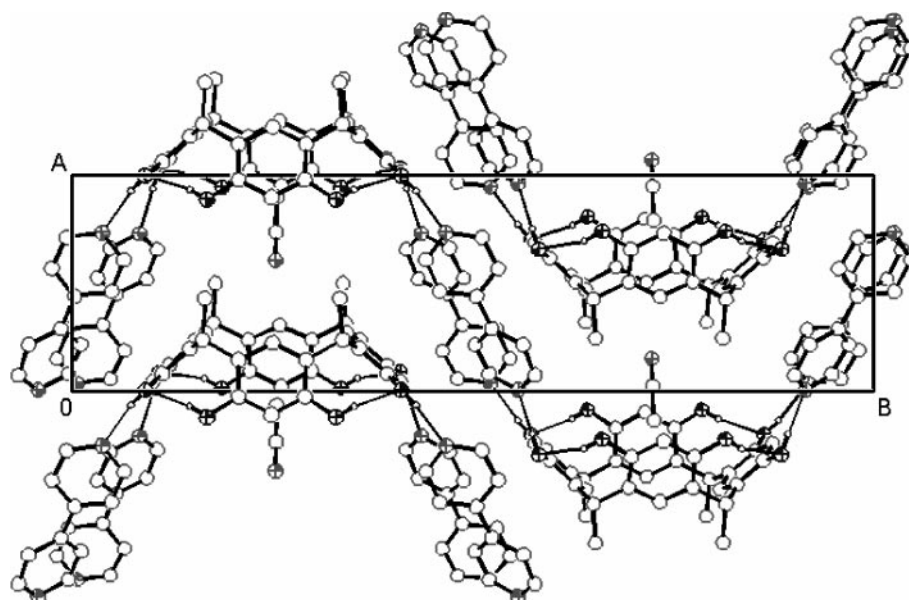


FIG. 5. X-ray crystal structure of  $3 \cdot 2(4,4'\text{-bipyridine}) \cdot \text{MeCN}$ .

within **3**, was also discovered (20). In particular, as shown in Fig. 6, cocrystallization of **3** with 4,4'-bipyridine from THF and THF/MeCN (8:1) yielded 1D wave-like arrays,  $3 \cdot 2(4,4'\text{-bipyridine}) \cdot \text{guest}$  (where guest = 2(THF), THF · MeCN, respectively), in which the dipole moments of the included guests are aligned in an approximate anti-parallel fashion, an orientation which presumably maximizes attractive electrostatic forces between constituent molecules.

To the best of our knowledge, these multiguest systems represent the first examples in which two guests have been isolated within a either a resorcin[4]arene or a calix [4]arene and suggest a possibility of using this framework

as a host for guests capable of undergoing reactions in the solid state.

#### LARGE CONTAINER ASSEMBLIES

It is clear that cocrystallization of **3** with pyridine and its derivatives in the presence of a suitable guest results in the elaboration of the cavity of **3** in which four pyridine units assemble along the upper rim of **3**, as two stacked dimers, to yield a multicomponent complex **5** in which **3** serves as a quadruple hydrogen bond donor (7, 16, 17, 19, 20).

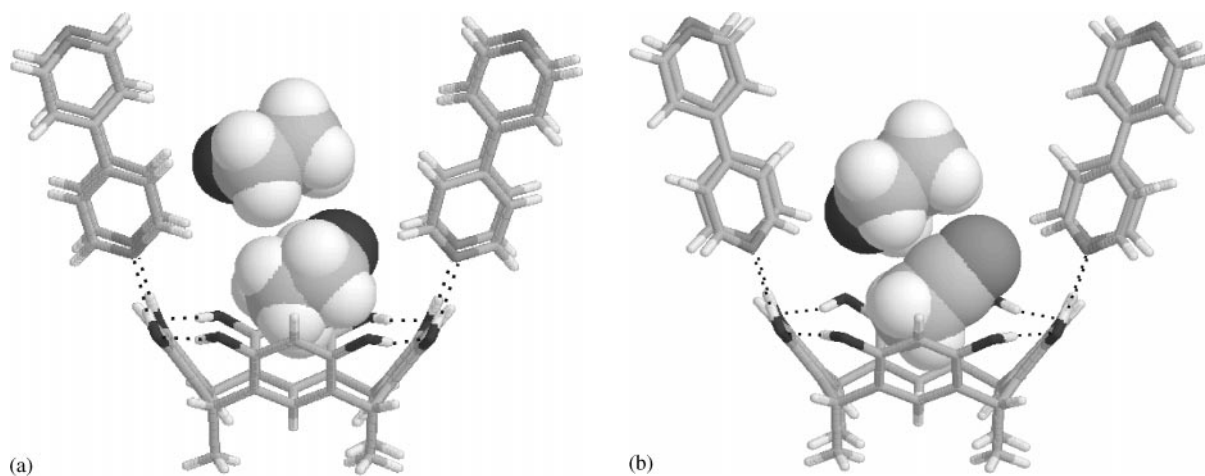


FIG. 6. X-ray crystal structure of (a)  $3 \cdot 2(4,4'\text{-bipyridine}) \cdot 2(\text{THF})$  and (b)  $3 \cdot 2(4,4'\text{-bipyridine}) \cdot \text{THF} \cdot \text{MeCN}$ .

### A Spherical Molecular Assembly

During studies aimed at cocrystallizing **3** with pyridines from aromatic solvents—potential guests for **5** (e.g., nitrobenzene)—we discovered the ability of **3** to self-assemble in the solid state, along with eight water molecules, to form a chiral spherical container assembly, with idealized octahedral symmetry, which is held together by 60 O–H...O hydrogen bonds **7** (Fig. 1) (11). The assembly was found to self-assemble in the solid state such that neighboring molecules of **3** are organized in a tail-to-tail fashion which, in turn, gives rise to an interpenetrating body-centered cubic lattice with interstices between **3** occupied by disordered water and nitrobenzene solvent molecules. Notably, although guest species could be located within **7**, it was not possible to determine their identity from the X-ray experiment, presumably owing to the high symmetry of the host and high thermal motion within the cavity. Solution studies also revealed the ability of *C*-undecylcalix[4]resorcinarene to maintain the structure of **7** in apolar organic solvents such as benzene (11).

### Polyhedron Model—Snub Cube

With a rational approach to elaborating the cavity of **3** supramolecularly achieved, we turned to determining whether the spherical structure of **7** could be rationalized according to principles of solid geometry. To us, the ability of six molecules of **3** to self-assemble to form **7** was reminiscent of spherical viruses (6) (e.g., hepatitis B) and fullerenes (21) (e.g.,  $C_{60}$ ) in which identical copies of proteins and carbon atoms self-assemble to form spherical molecular structures having icosahedral symmetry and a shell-like enclosure. Along these lines, consultation of polyhedron models revealed the structure of **7** to conform to a snub cube, one of the 13 Archimedean solids (13), in which the vertices of the square faces correspond to the corners of **3** and the centroids of the eight triangles that adjoin three squares correspond to the eight water molecules. Moreover, owing to its classification as an Archimedean solid, we concluded that to rationally construct similar hosts, and materials based upon such hosts, one must consider the limited possibilities available in space for spherical frameworks, those being the 5 Platonic and 13 Archimedean solids.

### Platonic Solids

The Platonic solids comprise a family of five convex uniform polyhedra which possess cubic symmetry (i.e., 32, 432, or 532 symmetry) and are made of the same regular polygons (e.g., equilateral triangle, square) arranged in space such that the vertices, edges, and three coordinate directions of each solid, are equivalent (Fig. 7) (13). That there is a finite number of such polyhedra is due to the fact that there exists

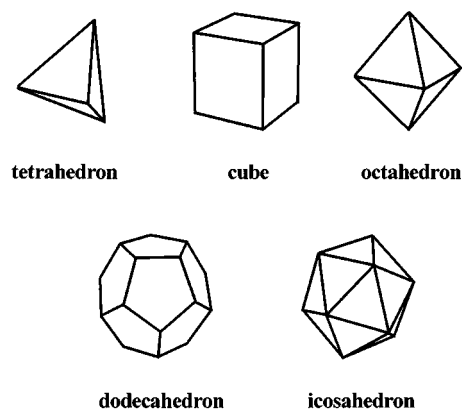


FIG. 7. The five Platonic solids.

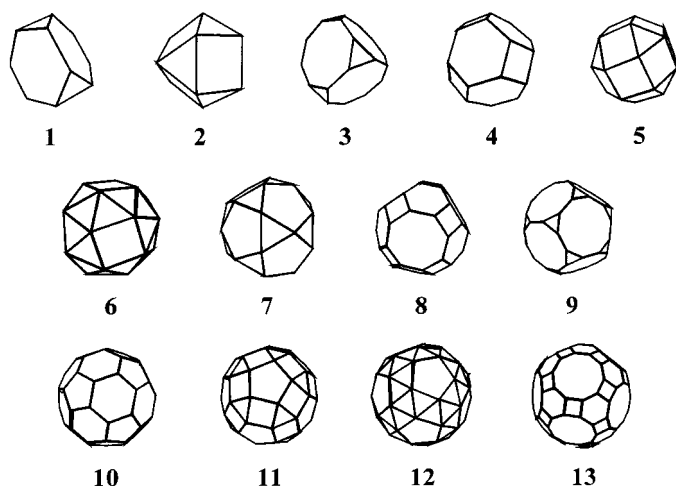
a limited number of ways in which identical regular polygons may be adjoined to construct a convex corner. Equilateral triangles may be adjoined in three ways while squares and pentagons may be adjoined in only a single manner. Moreover, it is impossible to create a convex corner using regular polygons with six or more sides since the sum of the angles around each vertex would be greater than or equal to  $360^\circ$  (13). These principles give rise to five isometric polyhedra which are achiral and whose polygons are related by combinations of  $n$ -fold rotation axes. The Platonic solids include the tetrahedron (point group  $T_d$ , 32 symmetry), the cube and octahedron (point group  $O_h$ , 432 symmetry), and the dodecahedron and icosahedron (point group  $I_h$ , 532 symmetry).

### Archimedean Solids

In addition to the Platonic solids, there exists a family of 13 convex uniform polyhedra known as the Archimedean solids (Fig. 8). Each member of this family is made up of at least two different regular polygons and may be derived from at least one Platonic solid through either truncation or the twisting of faces (13). In the case of the latter, two chiral members, the snub cube and the snub dodecahedron, are realized. The remaining Archimedean solids are achiral. Like the Platonic solids, the Archimedean solids possess identical vertices and exhibit either 32, 432, or 532 symmetry, respectively. The Archimedean solids possess a wider variety of polygons than the Platonic solids. These include the equilateral triangle, square, pentagon, hexagon, octagon, and decagon.

### Spherical Containers from the Laboratory and from Nature

Our contention that spherical molecular containers may be designed, in a similar way to **7**, according to principles of solid geometry renders organic and inorganic components viable for their design and permits the individual components



**FIG. 8.** The 13 Archimedean solids, in order of increasing number of vertices. Truncated tetrahedron (1), cuboctahedron (2), truncated cube (3), truncated octahedron (4), rhombicuboctahedron (5), snub cube (6), icosidodecahedron (7), rhombitruncated cuboctahedron (8), truncated dodecahedron (9), truncated icosahedron (10), rhombicosidodecahedron (11), snub dodecahedron (12), rhombitruncated icosidodecahedron (13).

of the host to be held together by covalent and/or non-covalent bonds. To demonstrate the utility of this approach, we will now present here selected examples of spherical hosts composed of organic components from both the laboratory and nature. We believe that such a symmetry-based approach permits the identification of similarities at the structural level which, at the chemical level, may not seem obvious and may be used to design assemblies similar to **7** (22).

### Platonic Solids

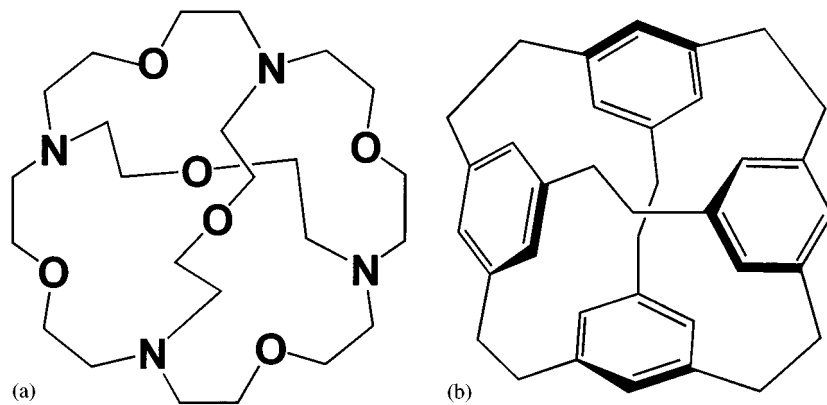
As stated, the Platonic solid constitute a family of five convex uniform polyhedra made up of the same regular polygons and possess either 32, 432, or 532 symmetry.

**Tetrahedral systems.** The macrotricyclic spherand designed by Lehn *et al.* was the first host with tetrahedral symmetry (Fig. 9a) (23). The bridgehead nitrogen atoms, located at the corners of the tetrahedron, and ethyleneoxy units, the edges, supply the threefold and twofold rotation axes, respectively. Notably, this molecule and its tetraprotonated form is able to bind an ammonium and chloride ion, respectively. Schmidtchen *et al.* have introduced similar tetrahedral cages with edges composed entirely of methylene bridges (24) while Vögtle *et al.* have demonstrated the synthesis of a hollow hydrocarbon called spheriphane (Fig. 9b) (25).

**Octahedral systems.** An example of an octahedral system is a cyclophane-based molecule reported by Murakami *et al.* (Fig. 10) (26). The sides of the host consist of tetraaza-[3.3.3.3]paracyclophane units and its octaprotonated cation has been shown to bind anionic guests.

A second is a cube synthesized by Chen and Seeman, the components of which are based upon DNA (27). The directionality and ability of the double helix to form branched junctions are exploited for the edges and vertices, respectively. Interestingly, each face of this DNA-based system forms a cyclic strand which is catenated with strands of adjacent faces. Molecular modeling experiments indicate the length of each edge to be approximately 6.8 nm.

**Icosahedral systems.** Spherical viruses are icosahedral molecular hosts related to the Platonic solids (Fig. 11a) (6). Consisting of identical copies of proteins which assemble, in a similar way to **7**, by way of noncovalent forces, these hosts range from 15 to 90 nm in diameter and encapsulate strands of ribonucleic acid (RNA). Although the shells of spherical viruses require a minimum of 60 subunits, most are made up of  $60n$  ( $n = 1, 3, 4 \dots$ ) subunits owing to a reduction in symmetry of their polygons (Fig. 11b). This process, known as triangulation, gives rise to quasi-equivalent positions along the surface of the shell which enable the virus particle



**FIG. 9.** Tetrahedral hosts with  $T_d$  symmetry: (a) Lehn's spherand, (b) Vögtle's spheriphane.



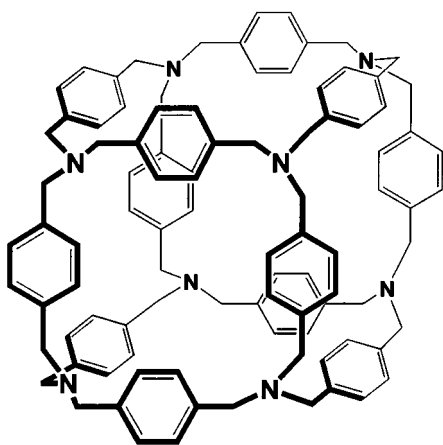


FIG. 10. Murakami's cyclophane-based cube.

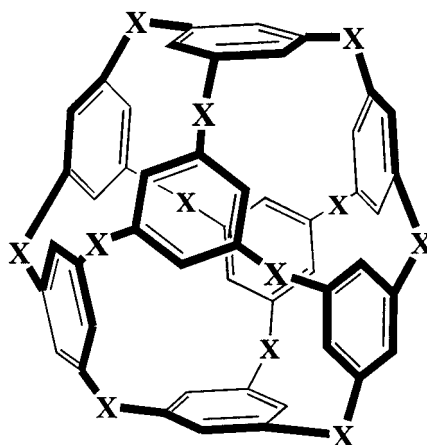


FIG. 12. A theoretical organic shell based upon the cuboctahedron (X = O, S).

to cover the RNA with the largest number of subunits. Since only certain triangulations are permitted by symmetry, viruses may be classified into a coherent system (6).

#### Archimedean Solids

As stated, the Archimedean solids constitute a family of 13 convex uniform polyhedra made up of two or more regular polygons and, like the Platonic solids, possess either 32, 432, or 532 symmetry.

*Cuboctahedron (2).* Ross *et al.*, using MM2 molecular model simulations, have considered the existence of a molecule containing eight benzene rings and either 12 oxygen or sulfur atoms which they refer to as heterospherophane (Fig. 12) (28). Although it is not mentioned in the original

report, the shell exhibits a topology identical to that of a cuboctahedron.

*Truncated octahedron (4).* Seeman and Zhang have constructed a DNA-based shell analogous to a truncated octahedron. The edges of this molecule, each of which contains two turns of the double helix, contain 1440 nucleotides and the molecular weight of the structure, which is an overall 14-catenane, is 790,000 Da (29). Interestingly, the design strategy relies on a solid support approach in which a net of squares is ligated to give the polyhedron. It is currently unclear what shape the molecule adopts in various media.

*Snub cube (6).* As stated, we have demonstrated the ability of six molecules of **3** and eight molecules of H<sub>2</sub>O to assemble in apolar media to form a spherical molecular

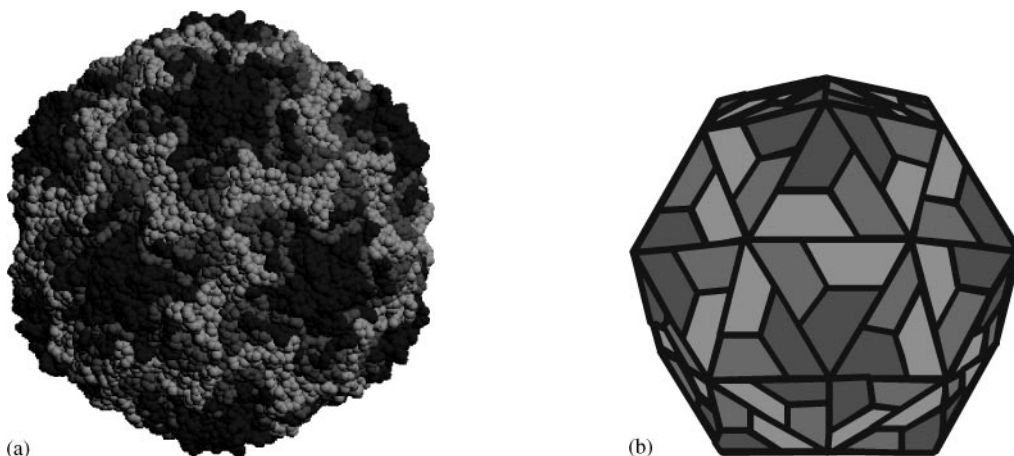


FIG. 11. An icosahedral host: (a) X-ray crystal structure of the rhinovirus, a spherical virus linked to the common cold, (b) a schematic representation of the rhinovirus displaying triangulation.

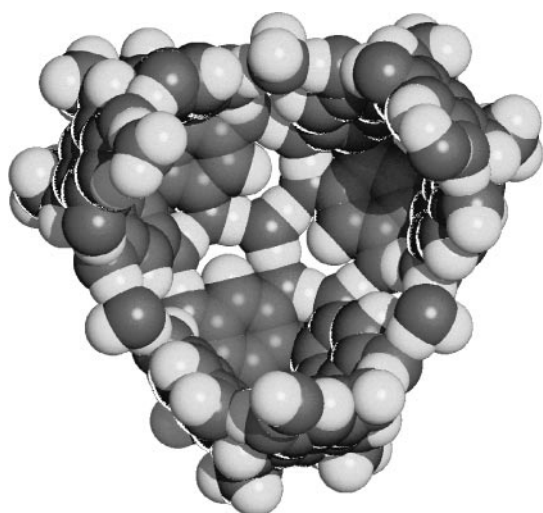


FIG. 13. Space-filling view of the cavity of **7**.

assembly which conforms to a snub cube (Fig. 13) (11). Each resorcin[4]arene lies on a fourfold rotation axis and each  $\text{H}_2\text{O}$  molecule on a threefold axis. The assembly, which exhibits an external diameter of 2.4 nm, possesses an internal volume of about  $1.4 \text{ \AA}^3$  and is held together by 60  $\text{O-H} \cdots \text{O}$  hydrogen bonds.

*Truncated icosahedron (10).* Buckminsterfullerene, an allotrope of carbon, is topologically equivalent to a truncated icosahedron, an Archimedean solid that possesses 12 pentagons and 20 hexagons (Fig. 14) (21). Each carbon atom of this fullerene corresponds to a vertex of the polyhedron. As a result,  $\text{C}_{60}$  is held together by 90 covalent bonds, the number of edges of the solid.

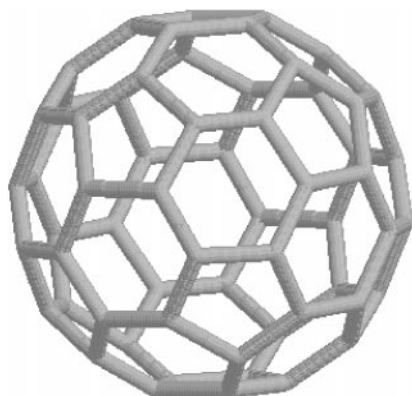


FIG. 14. X-ray crystal structure of buckminsterfullerene,  $\text{C}_{60}$ , a shell based upon the truncated icosahedron.

### Archimedean Duals and Irregular Polygons

As stated, the Platonic and Archimedean solids comprise two finite families of polyhedra in which each solid consists of identical vertices, edges, and either a single or two or more regular polygons. It is of interest to note, however, that there exists a family of spherical solids which are made up of irregular polygons which may also be used as models for spheroid design. Known as Archimedean duals (13), these polyhedra are constructed by simply connecting the midpoints of the faces of an Archimedean solid. Such a treatment gives rise to 13 polyhedra which possess two or more different vertices and identical irregular polygon faces (Fig. 15). As a result, chemical subunits used to construct hosts which conform to these polyhedra cannot be based upon regular polygons.

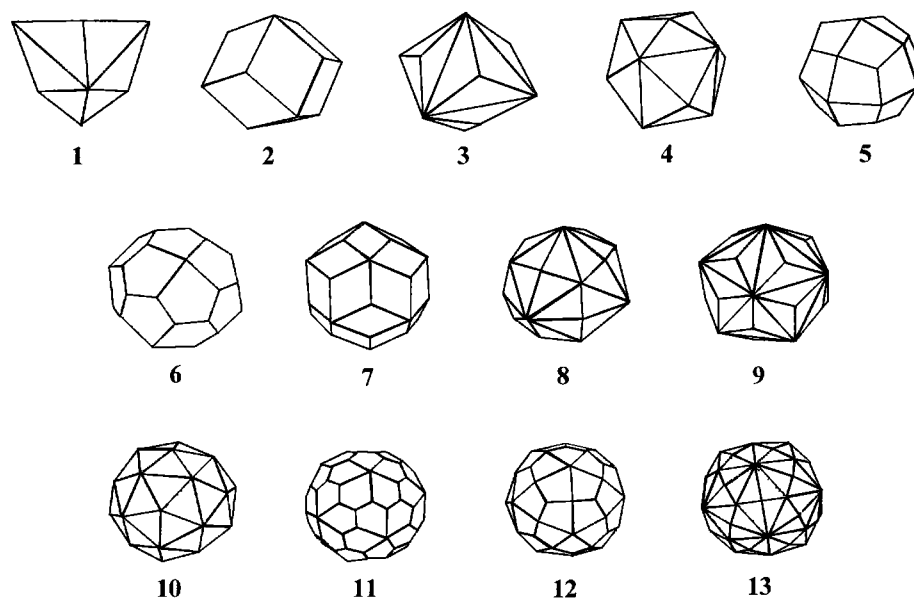
*Rhombic dodecahedron (2).* To the best of our knowledge, there is one host which conforms to the structure of an Archimedean dual. Harrison was the first to point out that the quaternary structure of ferritin, a major iron storage protein in animals, bacteria, and plants, corresponds to the structure of a rhombic dodecahedron (30). This protein, which is approximately 12.5 nm in diameter, consists of 24 identical polypeptide subunits (Fig. 16a), and holds up to 4500 iron atoms in the form of hydrated ferric oxide with varying amounts of phosphate  $[\text{Fe}_2\text{O}_3(\text{H}_2\text{O}/\text{H}_3\text{PO}_4)_n]$  (31). The polypeptides, which consist of four helix bundles, assemble by way of noncovalent forces and form dimers which correspond to the faces of the solid (Fig. 16b).

### Irregular polygons

It is important to point out that if partial truncation is applied to the Platonic solids such that Archimedean solids are not realized, or if truncation is applied to the Archimedean solids, then the resulting polyhedra will not possess regular faces but, like the Archimedean duals, may be used as models for spheroid design as a consequence of their cubic symmetries. Indeed, of the spherical hosts synthesized to date, all have been constructed using chemical subunits which either correspond to regular polygons (e.g., calix[4]arenes) or form regular polygons (e.g., carbon-based hexagons and pentagons). Moreover, that spherical shells may be constructed using polyhedra with irregular faces, as in the case of ferritin, implies that spherical shells based upon irregular polygons may be rationally designed.

### CONCLUSIONS

We have presented two general approaches for designing hydrogen bonded cavity-containing assemblies based upon **3**. By exploiting the ability of **3** to function as a quadruple hydrogen bond donor, we have shown that **3** may either



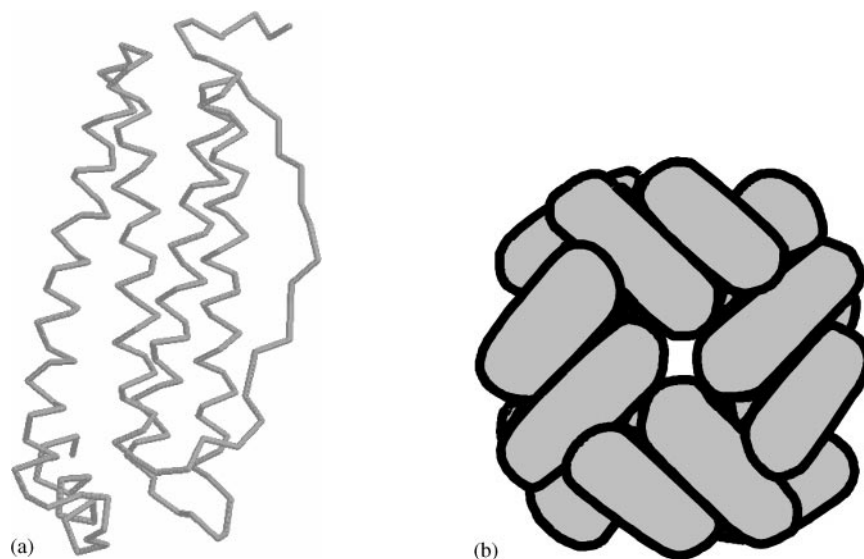
**FIG 15.** The 13 Archimedean duals derived from corresponding Archimedean solids (see Fig. 6). Triakis tetrahedron (1), rhombic dodecahedron (2), triakis octahedron (3), tetrakis hexahedron (4), deltoidal icositetrahedron (5), pentagonal icositetrahedron (6), rhombic tricontahedron (7), disdyakis dodecahedron (8), triakis icosahedron (9), pentakis dodecahedron (10), deltoidal hexecontahedron (11), pentagonal hexecontahedron (12), disdyakis triacontahedron (13).

assemble with itself or aromatic-based hydrogen bond acceptors to form multicomponent hosts that display molecular recognition properties analogous to monomolecular predecessors.

Specifically, the ability of pyridine and its derivatives, to deepen the cavity of **3** has been demonstrated (7, 16, 17, 19, 20) while **3** has been observed to self-assemble as a spherical hexamer, along with eight water molecules, to

form a container assembly held together by 60 hydrogen bonds (11). In the case of the latter, the host conforms to the structure of a snub cube, one of the 13 Archimedean solids, and a general strategy for the design of related spherical container assemblies has been developed (22).

With such observations realized, it is anticipated that, in addition to expanding the library of components used to construct these frameworks, focus will now be placed upon



**FIG. 16.** X-ray crystal structure of ferritin. A spherical host based upon the rhombic dodecahedron: (a) carbon trace of the polypeptide subunit, (b) the assembly displayed by the subunits.

incorporating higher levels of function (e.g., selectivity, chirality) within such materials in which case this molecular approach to materials design is expected to yield a diverse family of functional solids.

#### ACKNOWLEDGMENTS

We are grateful for funding from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the National Science Foundation (NSF).

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