Platonic and Archimedean Solids

Leonard R. MacGillivray
University of Iowa, Iowa City, Iowa, U.S.A.

INTRODUCTION

A molecular host that completely surrounds its guest provides a means to stabilize reactive and transient chemical intermediates, to transfer biologically active molecules to target cells, and to construct molecular-scale devices.[1–3] To design such a host, such a shell requires positioning of organic and/or inorganic chemical subunits in space such that the topological relationship of its subunits approximates a hollow spherical shell *S* capable of packaging single or multiple guests (Fig. 1).[1] A simple design strategy for the construction of such a host involves utilizing principles of solid geometry, wherein the chemical subunits positioned along the surface of *S* conform to either a Platonic or an Archimedean solid.[1–3]

SPHERICAL HOSTS

A spherical virus (e.g., rhinovirus) is a familiar example of a spontaneous process of self-assembly that gives rise to a spherical shell with a closed cavity able to host atoms and molecules as guests.[1] Such a spherical structure is desirable, because it employs an economy of information, providing access to a shell with chemical subunits in identical chemical environments where surface area is at a minimum and strain energy is distributed evenly along the surface. Whereas nature utilizes identical chemical subunits in the form of proteins, which assemble by way of noncovalent forces (e.g., hydrogen bonds), to construct a spherical virus, chemists have a wide variety of organic and inorganic building blocks at their disposal that may be used to design atomic- and nanometer-scale shells held together by noncovalent or covalent bonds. In a similar way to a spherical virus, such a shell may be designed to exhibit a targeted property (e.g., catalysis). The targeted property may be less available, or completely inaccessible, by nature.

SPHEROID DESIGN

To construct a molecular host with a spherical structure, the framework must be designed so that the guest is centralized within a hollow spherical shell *S*.[1] From a chemical standpoint, such a framework, however, is impossible to design, because atoms and molecules are discrete entities, whereas the surface of *S* is uniform. Thus, to construct a spherical molecular host, one must consider the number of identical chemical subunits *n* for spheroid design and their placement along the surface of the shell.

SUBUNITS FOR SPHEROID DESIGN

The simplest host that may be constructed using chemical subunits that approximate a sphere is a shell based on $n=4$ subunits with a structure that conforms to a tetrahedron.[4] Such a shell consists of four identical subunits in the form of equilateral triangles, where edge-sharing by the triangular faces provides the curvature along the surface of the shell. The polygonal subunits of the tetrahedron are related by combinations of twofold and threefold rotation axes such that the framework is of cubic symmetry (i.e., 32 symmetry).

PLATONIC SOLIDS

The tetrahedron belongs to a closed family of five convex uniform polyhedra known as the Platonic solids (Fig. 2), named after the ancient Greek philosopher Plato (circa 427–347 BC),[5] who speculated that the five solids were the shapes of the fundamental components of the universe. Each member of this family possesses cubic symmetry (i.e., 32, 432, or 532 symmetry) and is made of the same regular polygons (e.g., equilateral triangle, square) arranged in space so that its vertices and edges, and three coordinate directions, are equivalent. That there is a finite number of such polyhedra is a consequence of the fact that a limited number of ways exist 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. These principles give rise to five isometric polyhedra that are achiral, with polygons that are related by combinations of *n*-fold rotation axes. The Platonic solids include the tetrahedron, which belongs to the point group T_d and possesses 32 symmetry; the cube and octahedron,

DOI: 10.1081/E-ESMC 120012767

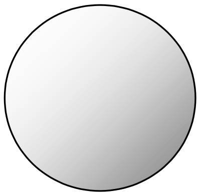


Fig. 1 Hollow spherical shell *S*.

which belong to the point group O_h and possess 432 symmetry; and the dodecahedron and icosahedron, which belong to the point group I_h and possess 532 symmetry.

ARCHIMEDEAN SOLIDS

In addition to the Platonic solids, a family of 13 convex uniform polyhedra known as the Archimedean solids (Fig. 3) exist, first described by the Greek philosopher Archimedes (287–211 or 212 BC).[6] The original work was lost and was reported second-handedly by Pappus of Alexandria (290–350), a Greek geometer. Each member of this family of solids is made up of at least two different regular polygons and may be derived from at least one Platonic solid through either truncation or twisting of faces. In the case of the latter, two chiral members, the snub cube and the snub dodecahedron, are realized. Like the Platonic solids, the Archimedean solids possess identical vertices and exhibit 32, 432, or 532 symmetry. The Archimedean solids exhibit a larger variety of polygons than the Platonic solids. These include the equilateral triangle, square, pentagon, hexagon, octagon, and decagon.

MODELS FOR THE DESIGN OF SPHERICAL MOLECULAR HOSTS

With a synthetic scheme for designing spherical shells based on principles of solid geometry realized, chemists exploited such geometric principles for the synthesis of spherical hosts that encapsulate atoms and molecules as guests.[1–3] In serving as models for the construction of spherical hosts, the Platonic and Archimedean solids provide a means with which to determine where chemical subunits should be placed along the surface of *S* and the bonding arrangements they should adopt. To demonstrate these principles, examples of spherical molecular hosts derived from the laboratory and nature will be described.

Platonic Solids

As stated, the Platonic solids constitute a family of five convex uniform polyheda made up of the same regular polygons and possessing 32, 432, or 532 symmetry.

Tetrahedral hosts

The macrotricyclic spherand designed by Lehn was the first tetrahedral host (Fig. 4a).[7] The bridgehead nitrogen atoms and ethyleneoxy units supply the threefold and twofold rotation axes, respectively. This molecule, and its tetraprotonated form, was shown to bind an ammonium and chloride ion, respectively.

Saalfrank was the first to introduce metal-based tetrahedral cages by using metal ions as corner units and bridging malonate ligands as edges (Fig. 4b).[8] Owing to a bend in each ligand, these cages are adamantane-like. In terms of host–guest behavior, an iron-based system was shown to complex a single ammonium ion.

Octahedral hosts

A cyclophane-based system reported by Murakami was shown to conform to a structure of a cube (Fig. 4c).[9] The sides of the host consist of tetraaza-[3.3.3.3]paracyclophane units, and its octaprotonated cation was shown to bind anionic guests. A polyoxovanadate, $(VO_6)(RPO_3)_8]^+$ (R=*t*Bu,OSiMe$_3$), reported by Zubieta[10] and Thorn,[11] was also shown to adopt an octahedral framework (Fig. 4d). The vanadium atoms of the shell are located at the vertices of an octahedron, while the phosphorus atoms are located at the corners of a cube. A cube with a structure based on deoxyribonucleic acid (DNA) was described by Seeman (Fig. 4e).[12] The directionality and ability of the double helix to form branched junctions were exploited for the edges and vertices, respectively.

Icosahedral hosts

Spherical viruses, found in nature, are examples of molecular hosts related to an icosahedron (Fig. 4f).[1] Possessing identical copies of proteins that assemble by

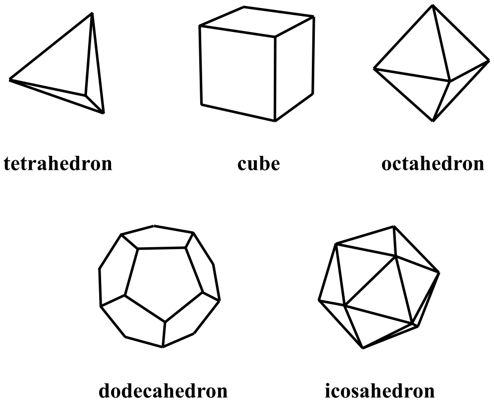


Fig. 2 The five Platonic solids.

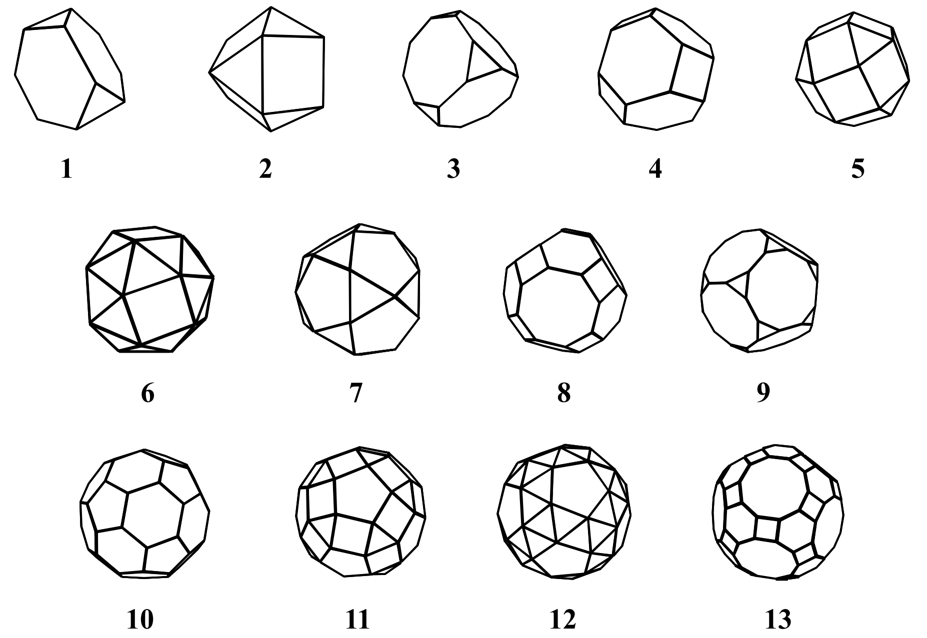


Fig. 3 The 13 Archimedean solids. Truncated tetrahedron (1), cuboctahedron (2), truncated cube (3), truncated octahedron (4), rhombicuboctahedron (5), snub cube (6), icosidodecahedron (7), rhombitruncated cuboctahedron (8), truncated dodecahedron (9), truncated icosahedron (10), rhombicosidodecahedron (11), snub dodecahedron (12), and rhombitruncated icosidodecahedron (13).

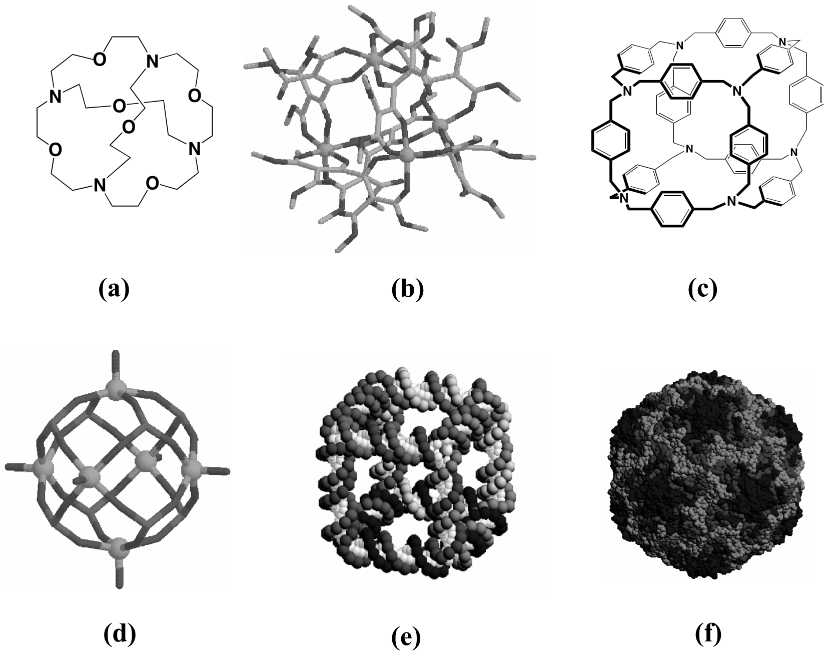


Fig. 4 Spherical hosts based on the Platonic solids: (a) spherand (tetrahedron); (b) metal-organic cage (tetrahedron); (c) cyclophane-based cube (cube); (d) the $[(VO_6)(RPO_3)_8]^+$ ion (R=*t*Bu, $OSiMe_3$) (octahedron and cube); (e) DNA-based cube (printed with permission by Professor Nadrian Seeman) (cube); and (f) the rhinovirus (icosahedron). (*View this art in color at www.dekker.com.*)

way of noncovalent forces (e.g., hydrogen bonds), these hosts range from 15–90 nm in diameter and encapsulate strands of ribonucleic acid.

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 32, 432, or 532 symmetry.

Truncated tetrahedron

Fujita,[13] Stang,[14] and Steel[15] described metal-organic cages that are topologically analogous to a truncated tetrahedron (Fig. 5a). These systems consist of metal ions and aromatic-based bridging ligands that constitute the twofold and threefold rotation axes, respectively. In terms of host–guest behavior, x-ray crystallographic studies revealed the assembly reported by Fujita to form a complex with four adamantyl carboxylate ions, while that reported by Steel to encapsulate a molecule of dimethylsulfoxide. According to mass spectrometric data, the cage described by Stang associates with four triflate ions.

Cuboctahedron

Gonzàlez-Duarte described the ability of eight cadium ions and 16 thiolate ligands to assemble to form a highly charged cage, $[\mathrm{ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}}]^{15+}$, the sulfur atoms of which sit at the vertices of a cuboctahedron.[16] The host contains a central chloride ion and an inner tetrahedral array of cadmium ions. A large metal-organic shell that conforms to a cuboctahedron and is based upon Cu(II) ions that assemble with a triazo ligand was described by Robson.[17] The shell possesses a cavity with a volume of approximately 816 Å^3 and is speculated to accommodate five to six molecules of dimethylformamide.

Truncated octahedron

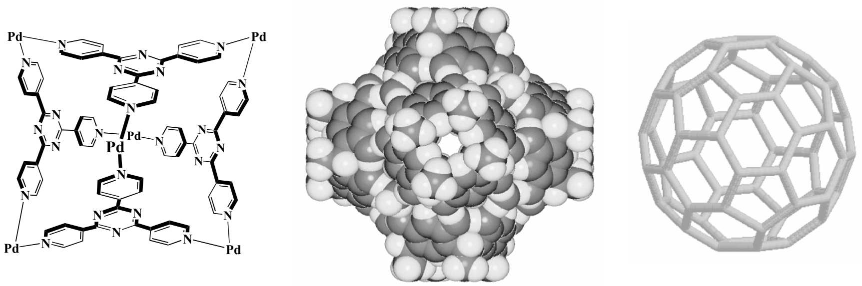
Seeman constructed a DNA-based shell analogous to a truncated octahedron.[18] The edges of this molecule, each of which contains two turns of the double helix, contain 1440 nucleotides. The molecular weight of the structure, which is an overall 14-catenane, is 790,000 Daltons. The design strategy relied on a solid support approach, where a net of squares is ligated to give the polyhedron.

Rhombicuboctahedron

Müller showed that 24 oxygen atoms of the polyoxometalate $[\mathrm{As_4Mo_6V_7O_{39}}]^{2-}$ may be attributed to the structure of a rhombicuboctahedron.[19] A strong ‘‘tetrahedral distortion’’ of each ion is required to correspond each host to the polyhedron. This shell was shown to complex a sulfate ion in the solid state.

Snub cube

MacGillivray and Atwood demonstrated the ability of six resorcin[4]arenes and eight water molecules to assemble in apolar media to form a spherical molecular assembly that conforms to a snub cube (Fig. 5b).[20] Each resorcin[4]arene lies on a fourfold rotation axis and each H_2O molecule on a threefold axis. The vertices of the square faces of the polyhedron correspond to the corners of the resorcin[4]arenes and the centroids of the eight triangles that adjoin three squares correspond to the water molecules. The assembly, which exhibits an external diameter of 2.4 nm, possesses an internal volume of about 1400 Å^3 and is held together by 60 O–H···O hydrogen bonds.



(a) **(b)** **(c)**

Fig. 5 Spherical hosts based on the Archimedean solids: (a) metal-organic cage (truncated tetrahedron), (b) calix[4]resorcinarene spheroid (snub cube), and (c) buckminsterfullerene (truncated icosahedron). (*View this art in color at www.dekker.com.*)

Truncated icosahedron

Buckminsterfullerene, an allotrope of carbon, is topologically equivalent to a truncated icosahedron, an Archimedean solid based on 12 pentagons and 20 hexagons (Fig. 5c).[21] Each carbon atom of the framework corresponds to a vertex of the polyhedron. As a result, C_{60} is held together by 90 covalent bonds, the number of edges of the solid.

CONCLUSION

Although chemists demonstrated an ability to utilize principles of solid geometry to design spherical hosts that encapsulate atoms and molecules, it is clear that much work remains to be accomplished. Indeed, although there exists a limited number of ways (i.e., Platonic and Archimedean solids) in which polygons may be arranged to enclose space, that chemists are able to mimic such structures chemically means that, in principle, an unlimited number of shells, with sizes that range from the angstrom—to the nanometer-scale level, and beyond (i.e., >10 Å), may be constructed. Moreover, a recent report by Swiegers illustrated that a classification system that accounts for different assembly processes available for a given polyhedron is feasible, meaning that a variety of routes to Platonic and Archimedean structures remain unexplored.[22] Notably, whereas nature utilizes template-directed synthesis to form the polypeptide chains that assemble to form a spherical virus, chemists utilized a fundamentally different approach to synthesis that relies on diffusion-controlled synthesis to construct the subunits of spherical hosts.[23] Moreover, an ability of chemists to mimic such template-controlled processes could provide access to spherical hosts with properties not accessible using a more classical approach synthesis. The imagination of the chemist, concomitant with an understanding of principles of biology and geometry, will lead to further advances in this area.

ARTICLES OF FURTHER INTEREST

Anion-Directed Assembly, p. 51
Calixarenes and Their Analogues: Cation Complexation, p. 137
Calixarenes and Their Analogues: Molecular Complexation, p. 145
Carcerands and Hemicarcerands, p. 189
Cavitands, p. 219
Chiral Guest Recognition, p. 236
Crown Ethers, p. 326
Cryptands, p. 334
Cryptophanes, p. 340
Cucurbituril, Its Homologues, and Derivatives, p. 390
Cyclodextrins, p. 398
Cyclophanes: Endoacidic, Endobasic, and Endolipophilic Cavities, p. 424
DNA Nanotechnology, p. 475
Fullerenes as Encapsulating Hosts: Preparation, Detection, and Structures of Endohedral Fullerenes, p. 579
Glycoluril-Based Hosts, p. 597
Homocalixarenes, p. 649
The Lock and Key Principle, p. 809
Macrocycle Synthesis, p. 830
Molecular Squares, Boxes, and Cubes, p. 909
Platonic and Archimedean Solids, p. 1100
Preorganization and Complementarity, p. 1158
Self-Assembling Capsules, p. 1231
Self-Assembly: Terminology, p. 1263
Solvation Effects in Guest Binding, p. 1322
Spherands, p. 1344
Viruses as Host Assemblies, p. 1563

REFERENCES

1. MacGillivray, L.R.; Atwood, J.L. Structural classification and general principles for the design of spherical molecular hosts. Angew. Chem., Int. Ed. Engl. **1999**, *38*, 1018–1033.
2. Leininger, L.; Olenyuk, B.; Stang, P.J. Self-assembly of a discrete cyclic nanostructure mediated by transition metals. Chem. Rev. **2000**, *100*, 853–908.
3. Caulder, D.L.; Raymond, K.N. The rational design of high symmetry coordination clusters. Dalton Trans. **1999**, 1185–1200.
4. Holden, A. *Shapes, Space, and Symmetry*; Columbia University Press: New York, 1971.
5. Plato. *Timaeus*; Warrington, J., Ed.; Dent: London, 1965. Original c. 360 B.C.
6. Wenninger, M.J. *Polyhedron Models*; Cambridge University Press: New York, 1971.
7. Graf, E.; Lehn, J.-M. Cryptates. XVII. Synthesis and cryptate complexes of a spheroidal macrotricyclic ligand with octahedrotetradral coordination. J. Am. Chem. Soc. **1975**, *97*, 5022–5024.
8. Saalfrank, R.W.; Stark, A.; Peters, K.; von Schnering, H.G. Adamantanoid chelate complexes. 1. The first adamantanoid alkaline earth metal chelate complex: Synthesis, structure, and reactivity. Angew. Chem., Int. Ed. Engl. **1988**, *27*, 851–853.
9. Murakami, Y.; Hayashida, O. Supramolecular effects and molecular discrimination by macrocyclic hosts embedded in synthetic bilayer membranes. Proc. Natl. Acad. Sci. U.S.A. **1993**, *90*, 1140–1145.
10. Salta, J.; Chen, Q.; Chang, Y.D.; Zubieta, J. The

oxovanadium organophosphonate system: $(VO)_6(tert\text{-}C_4H_9PO_3)_8Cl]$, $[(VO)_4\{PhP(O)_2OP(O)_2Ph\}_4Cl]$-, and $[V_{18}O_{25}(H_2O)_2(PhPO_3)_{20}Cl_4]^{4-}$, complex cluster structures with chloride ions inclusion from simple precursors. Angew. Chem., Int. Ed. Engl. **1994**, *33*, 757–760.

11. Thorn, D.L.; Harlow, R.L.; Herron, N. Phosphatovanadium chemistry: New compounds, including an example of ''Tenne's prospect,'' and oxidation of cyclohexadiene. Inorg. Chem. **1995**, *34*, 2629–2638.
12. Chen, J.; Seeman, N.C. Synthesis from DNA of a molecule with the connectivity of a cube. Nature **1991**, *350*, 631–633.
13. Fujita, M.; Oguro, D.; Moyazawa, M.; Oka, H.; Yamaguchi, K.; Oguro, K. Self-assembly of ten molecules into nanometre-sized organic host frameworks. Nature **1995**, *378*, 469–471.
14. Stang, P.J.; Olenyuk, B.; Muddiman, D.C.; Smith, R.D. Transition-metal-mediated rational design and self-assembly of chiral, nanoscale supramolecular polyhedra with unique T symmetry. Organometallics **1997**, *16*, 3094–3096.
15. Hartshorn, C.M.; Steel, P.J. Self-assembly and x-ray structure of a ten-component, three-dimensional metallosupramolecular cage. Chem. Commun. **1997**, 541–542.
16. Gonzàlez-Duarte, P.; Clegg, W.; Casals, I.; Sola, J.; Rius, J. Unprecedented polycrystal structure of a new cadmium thiolate containing an unusually highly charged $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ core. J. Am. Chem. Soc. **1998**, *120*, 1260–1266.
17. Abrahams, B.F.; Egan, S.J.; Robson, R. A very large metallosupramolecular capsule with cube-like 43 topology assembled from twelve Cu(II) centers and eight tribidentate tri-anionic ligands derived from 2,4,6-triphenylazo-1,3,5-trihydroxybenzene. J. Am. Chem. Soc. **1999**, *121*, 3535–3536.
18. Zhang, Y.; Seeman, N.C. Construction of DNA-truncated octahedron. J. Am. Chem. Soc. **1994**, *116*, 1661–1669.
19. Müller, A.; Krickemeyer, E.; Dillinger, S.; Bögge, H.; Stammler, A. $As_4Mo_6V_7O_{39}(SO_4)^{4-}$: A species with an unusual structure and a model for the different host–guest properties of poly-vanadates and -molybdates. J. Chem. Soc. Chem. Commun. **1994**, 2539–2540.
20. MacGillivray, L.R.; Atwood, J.L. A chiral spherical molecular assembly held together by 60 hydrogen bonds. Nature **1997**, *369*, 469–472.
21. Kroto, H.W.; Heath, J.R.; O'Brien, S.C.; Curl, R.F.; Smalley, R.E. C_{60}: Buckminsterfullerene. Nature **1985**, *318*, 162–163.
22. Swiegers, G.F.; Malefetse, T.J. Classification of coordination polygons and polyhedra according to their mode of self-assembly. Chem. Eur. J. **2001**, *7*, 3637–3643.
23. Branden, C.; Tooze, J. *Introduction to Protein Structure*; Garland: New York, 1991.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016