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A Descriptor System and Principles for Numbering Closed Boron Polyhedra with at Least One Rotational Symmetry Axis and One Symmetry Plane

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A method for uniquely describing closed, fully triangulated, boron polyhedra with 4–24 vertices based on currently accepted procedures for numbering of coordination and boron polyhedra is proposed. Minor refinements and extensions to the numbering principles for closed polyhedra are suggested.

Introduction

Before Hawthorne and co-workers[2] pioneered the development of metallopolyboron chemistry, describing the structure of known closed polyboron hydride systems was not very difficult. At that time, it did not appear that there would be more than one polyhedral structure for each $[B_nH_n]^{2-}$ composition. Therefore, the descriptive prefix "clovo",[3] later modified to "*closo*-",[4] derived from the Greek word for cage, κλωβὸσ, was sufficient to identify these polyhedral structures and to distinguish them from the nonclosed, or open, polyboron hydride structures already known.[5]

The development of metallopolyboron chemistry has led to a need for a more extensive and definitive method for describing closed polyhedral structures. Incorporating metal atoms into polyboron hydride systems substantially increased the variety of closed polyhedral structures. Metallopolyboron chemistry led to the preparation of polyhedra with more than 12 vertices, the so-called supraicosahedra,[6,7] which, in turn, stimulated postulation of much larger polyhedra, containing as many as 32 vertices.[8] New structures for polyhedra with less than 12 vertices were also found in metalloboron systems.[9]

A more comprehensive system for describing closed polyhedral systems is also needed to provide the basis for naming many nonclosed polyboron structures, which often can be most effectively described as derived from closed polyboron systems. For example, metallopolyboron hydrides can be named as metal–ligand complexes in which the ligands are nonclosed anionic polyboron hydrides. Lack of a general system for describing a variety of nonclosed polyboron hydrides as anions or as anionic ligands led to the introduction of trivial names, such as ollide,[10a] zapide,[10b] and canastide,[10c] as well as new descriptive prefixes, such as "canasto-" and "anello-".[11] One of the easiest and most general methods for visualizing and describing these complex, often nonicosahedral, polyboron fragments is the "debor" method[4b] in which the nonclosed frameworks are specified by removing boron vertices from relatively more symmetrical closed polyhedra.[12]

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[1] (a) Chemical Abstracts Service. (b) The University of Chicago; Camille and Henry Dreyfus Teacher-Scholar.

[2] M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87** (8), 1818–1819 (1965).

[3] (a) J. Van Wazer, "Phosphorus and Its Compounds", Vol. 1, Interscience, New York, 1958, p 89; (b) R. M. Adams, *Inorg. Chem.*, **2** (6), 1087–1088 (1963); (c) R. M. Adams, *J. Chem. Doc.*, **5** (2), 95–98 (1965).

[4] (a) American Chemical Society, "The Nomenclature of Boron Compounds", *Inorg. Chem.*, **7** (10), 1945–1964 (1968); (b) International Union of Pure and Applied Chemistry, "Nomenclature of Inorganic Boron Compounds", *Pure Appl. Chem.*, **30** (3–4), 683–710 (1972).

[5] W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, 1963.

[6] (a) D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95** (4), 1109–1115 (1973); (b) W. J. Evans and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 38–39, 1974.

[7] (a) W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **99** (12), 4016–4029 (1977); (b) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **17** (1), 6–10 (1978).

[8] (a) L. D. Brown and W. N. Lipscomb, *Inorg. Chem.*, **16** (12), 2989–2996 (1977); (b) J. Bicerano, D. S. Marynick, and W. N. Lipscomb, *ibid.*, **17** (7), 2041–2042; **17** (12), 3443–3453 (1978).

[9] (a) K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97** (2), 296–302 (1975); (b) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **16** (12), 3255–3262 (1977); (c) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **98** (6), 1600–1601 (1976).

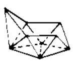
[10] (a) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Am. Chem. Soc.*, **90** (4), 879–896 (1968); (b) T. A. George and M. F. Hawthorne, *ibid.*, **91** (20), 5475–5482 (1969); (c) J. N. Francis and M. F. Hawthorne, *Inorg. Chem.*, **10** (4), 863–864 (1971).

[11] (a) "Gmelin Handbuch der Anorganischen Chemie", Vol. 15, Supplement, Boron Compounds 2, 8th ed., Springer-Verlag, Berlin, 1974, Chapter 1, pp 1–138. (b) W. Stumpf, *Chem. Z.* **99** (1), 1–12 (1975); (c) W. Stumpf, "Nomenclature, Compound Types and Chemistry of the Carboranes" in "Themen zur Chemie des Bors", H. Mollinger, Ed., Huthig Verlag GmbH, Heidelberg, 1976.

[12] The "debor" method allows for rather easy visualization and numbering of polyhedral fragments by treatment as closed polyhedral structures from which one or more specific vertices and their associated edges have been removed. For example, the $[B_8H_8]^{4-}$ ion can be described in terms of the tricapped trigonal prism from which one of the vertices of the trigonal prism has been removed. Further, the boron frameworks of the "normal" and "iso" nonaborane(15) isomers can be depicted in terms

$[B_8H_8]^{4-}$
framework

n-B_9H_{15}
framework



i-B_9H_{15}
framework

of the closed $[B_{11}H_{11}]^{2-}$ polyhedron from which two vertices have been removed: the highest coordination vertex first, followed by the highest or lowest coordination vertex, respectively, from the resulting hexagonal open face.

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Recent advances in the preparation of more irregular polyhedral metallopolyboron compounds[13] have emphasized the need for even more closed polyhedra, often hypothetical, from which nonclosed polyboron hydride frameworks can be generated. Although the "debor" system is the most general method yet proposed for describing polyhedral fragments, other techniques, such as the prefix "seco" used in organic nomenclature for indicating fission of rings,[14a] could be adapted to describe nonclosed polyboron hydride structures by derivation from appropriate closed polyhedra.[15] Obviously, methods for describing nonclosed polyboron frameworks based on closed polyhedra can only be as useful as the structural information given or implied by the name for the appropriate closed polyhedron. Hence, it is necessary to have a fully descriptive system not only to differentiate among various closed polyboron polyhedral structures with the same number of vertices but also to describe structures of an increasing number of nonclosed polyboron compounds.

Discussion

Although attempts have been made to specify polyhedral geometries both qualitatively[11,16a,17] and quantitatively,[18] a general system has not resulted. Recently, Brown and Lipscomb have published theoretical discussions on polyboron hydrides with more than 12 vertices,[8] which illustrate the inherent problems in identifying polyhedral frameworks. They list[8a] point group symmetry symbols, the total number of faces, edges, and vertices, the different types of vertices and edges, an "arrangement of vertices" following a method used by Föppl in a pre-quantum-mechanical description of electrons in atoms as points on a sphere,[19] and an "arrangement of vertices" with six skeletal near neighbors. From this tabulation it is clear that the point group symmetry symbol alone, or even when coupled with the number of vertices, edges, or faces, is not sufficient to differentiate between some polyhedra having the same number of vertices. For example, Brown and Lipscomb discuss two C_{2v} 17-vertex polyhedra, two C_s 19-vertex polyhedra, two C_{2v} 23-vertex polyhedra, and three D_{3d} 24-vertex polyhedra.[8a] The problem of distinguishing between polyhedra with the same number of vertices also has been recognized in polyhedra with less than 12 vertices.[20]

The "arrangement of vertices" listed by Brown and Lipscomb[8a] is also not sufficient, by itself, to distinguish between some polyhedra having the same number of vertices. However, their citation closely resembles the technique that has been used for numbering closed polyboron systems[4] as well as assigning locant designators in coordination polyhedra.[16b] Although not yet fully consistent, these two procedures agree in that the vertices of a polyhedron should be numbered in sequential planes perpendicular to a rotational symmetry axis of the polyhedron.

It occurred to us that structural information, such as that tabulated by Brown and Lipscomb,[8a] could be combined with the basic principles for numbering closed polyhedra[4] to form a descriptor that would uniquely define different polyhedra and also provide valuable assistance in visualizing the structure and in numbering the polyhedral vertices. Therefore, we propose a four-part structural descriptor for fully triangulated polyboron polyhedra (deltahedra) that have at least one rotational symmetry axis and at least one symmetry plane: (1) the point group symmetry symbol for the homogeneous polyboron framework; (2) a description of the arrangement and type of vertices, enclosed in parentheses or brackets; (3) a symbol giving the type and number of faces; and (4) the familiar descriptor "*closo-*".[4]

The *point group symmetry symbol* (Schoenflies symbol) is assigned on the basis of a homogeneous polyboron polyhedron from which substitutents and/or ligands have been removed from each vertex, since heteroatoms, particularly metallic heteroatoms, and certain substituents or ligands, can significantly distort the polyhedral structure. Furthermore, in order to be structurally significant, the symmetry symbol and the arrangement of vertices (see below) must be assigned on the basis of an idealized closed deltahedral structure. Construction of idealized models using only equilateral triangles leads to difficulties not only in physically constructing stable polyhedral models but also in visualizing equivalent polyhedral vertices, especially in larger polyhedra. As noted by Brown and Lipscomb,[8] boron-boron distances in real polyhedral boron compounds vary according to the skeletal connectivities of the boron atoms. Skeletal connectivity is the coordination number of the boron atom in the polyhedron; i.e., exopolyhedral bonding is not considered. Therefore, we have used different edge lengths in building models of the idealized triangulated polyhedra in this study. Our models were built with materials obtained from GEODESTIX, P.O Box 308, Parkwater Station, Spokane, Wash. 99211. An edge length of 76 mm (3 in.) was used for connections between polyhedral vertices with skeletal connectivities of 3, 4, and 5. Vertices with a skeletal connectivity of 5 were connected to vertices with skeletal connectivities of 6 or 7 by an edge length of 89 mm (3.5 in.). Connections between vertices with skeletal connectivities of 6 and 7 were 102 mm (4 in.) long. These edge lengths were quite satisfactory for all models of the polyhedra shown in Table I.

The part of the proposed descriptor giving the *arrangement and type of vertices* is most important since it provides very useful information for visualizing and building the polyhedral structure and for assigning locants (numbers) to its vertices. This segment consists of a series of Arabic numbers giving the number of vertices with the same skeletal connectivity, i.e., number of polyhedral edges associated with the vertex, in planes that are perpendicular to the reference axis of the polyhedron, i.e., the rotational symmetry axis that is preferred for numbering (see section on numbering, below). These primary Arabic numbers are cited *in the order* that the planes they define are preferred for numbering (see section on numbering, below). Each of these Arabic numbers is followed by the symbol v^n, where n is a superscript Arabic number giving the number of polyhedral edges associated with each of the vertices, i.e., the skeletal connectivity of each vertex. When

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(13) (a) W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **98** (12), 3490–3495 (1976); (b) W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *ibid.*, **99** (12), 4016–4029 (1977); (c) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **17** (1), 6–10 (1978); **18** (7), 1936–1940 (1979); (d) W. M. Maxwell and R. N. Grimes, *ibid.*, **18** (3), 2174–2178 (1979).

(14) International Union of Pure and Applied Chemistry, "Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F, and H", Pergamon Press, Oxford, 1979: (a) Rules C-16.1, p 108, and F-4.7, p 502; (b) Rules A-34, pp 25–27, and B-14, pp 75–76.

(15) L. A. Paquette, W. J. Begley, D. Balogh, M. J. Wyvratt, and D. Bremner, *J. Org. Chem.*, **44** (21), 3630–3638 (1979); *J. Am. Chem. Soc.*, **101** (3), 749–751 (1979).

(16) International Union of Pure and Applied Chemistry, "Nomenclature of Inorganic Chemistry (1970)," 2nd ed., Butterworths, London, 1971: (a) Table III, p 103; (b) Rule 7.514, p 63.

(17) (a) R. B. King, *J. Am. Chem. Soc.*, **91** (26), 7211–7216 (1969); **92** (22), 6460–6466 (1970); (b) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **13** (6), 1411–1418 (1974).

(18) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96** (6), 1748–1756 (1974).

(19) (a) L. Föppl, *J. Reine Angew. Math.*, **141**, 251 (1912); (b) L. Föppl, "Proceedings of the 5th International Congress on Mathematics," Vol. 2, Cambridge University Press, Cambridge, 1912, p 188.

(20) R. M. Adams, in a private communication, noted that both the monocapped octahedron and the tricapped tetrahedron have the point group symmetry symbol C_{3v}. D. M. P. Mingos, in a private communication, noted that there are two 11-vertex "noncapped" polyhedra with C_{2v} symmetry; see H-1 and H-2 in Table I.

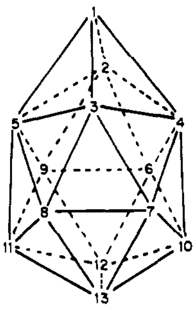

Figure 1. A 13-vertex polyhedron.

all vertices assigned to a plane do not have the same number of associated polyhedral edges, i.e., at least two v^n symbols are needed to describe the vertices in that plane, or when it is virtually impossible to determine the vertical order of planes of symmetrically equivalent vertices for citation and numbering, the Arabic numbers and their associated v^n symbols are enclosed in parentheses or brackets. Structures N-2, Q-3, T-1, U-3, and V-2 in Table I illustrate these situations. Although in most cases it should not be necessary to specify the precise arrangement of different vertices in the same plane because of the restrictions imposed by the requirement of a rotational symmetry axis, to be consistent with the principles of the descriptor, the first member within the parentheses includes the kind of vertex at which numbering begins in that plane. This part of the descriptor not only facilitates visualization of the polyhedral structure but also allows the locant numbers of the polyhedral vertices to be assigned quickly, without need to refer to all of the numbering rules. It also minimizes uncertainty about the assignment of various vertices to specific planes, as can occur occasionally; for example, see the polyhedron in Figure 5. Finally, although quite obvious, it should be noted that the sum of the primary Arabic numbers is the total number of vertices of the polyhedron.

Although a *symbol* for denoting the *type* and *number* of faces in a closed polyhedral structure might appear to be unnecessary in a system designed for deltahedral polyboron hydrides, it does serve to emphasize that the descriptor refers to polyhedra having only one kind of face. It also illustrates the generality of the system by providing a mechanism for using the same principles to describe polyhedral systems having uniform faces other than triangular. Polyhedral structures with all tetragonal, pentagonal, or hexagonal faces are known or have been postulated, although triangulated polyhedra (deltahedra) are by far the most common. An obvious symbol for indicating triangulated polyhedra is the captial Greek letter delta, Δ, or some simple reorientation of this character, as has been suggested.[21] Tetragonal- and pentagonal-faced polyhedra could be denoted by appropriate symbols for the square and pentagon, respectively. The number of faces is specified conveniently by adding an appropriate superscript Arabic number to such symbols. Thus, the icosahedral deltahedron would be denoted by the symbol Δ^{20} and the cube by $\square^6$.

The complete descriptor for the 13-vertex polyhedron shown in Figure 1 is $[C_{2v}\text{-}(1v^4 2v^5 2v^6 4v^5 2v^5 2v^5)\text{-}\Delta^{22}\text{-}closo]$.

The descriptor, as proposed, is quite comprehensive, and any attempts to simplify it should be considered very carefully so that its generality will not be impaired. However, for boron polyhedra, and perhaps for all fully triangulated polyhedra, we believe it would be permissible to omit the v^n symbol when $n = 5$. Accordingly, the descriptor for the 13-vertex polyhedron in Figure 1 would become $[C_{2v}\text{-}(1v^4 22v^6 422)\text{-}\Delta^{22}\text{-}closo]$. It may also be convenient to omit the v^n symbol when $n = 3$ and 4 for the common polyhedra with 12 or fewer vertices. Thus, the descriptor for the D_{2d} dodecahedron shown as E-1 in Table I could be $[D_{2d}\text{-}(2222)\text{-}\Delta^{12}\text{-}closo]$ rather than $[D_{2d}\text{-}(2v^4 222v^4)\text{-}\Delta^{12}\text{-}closo]$. The proposed structural descriptors, including only the omission of the v^5 symbol, and the numbering for 45 closed polyhedral systems are given in Table I.

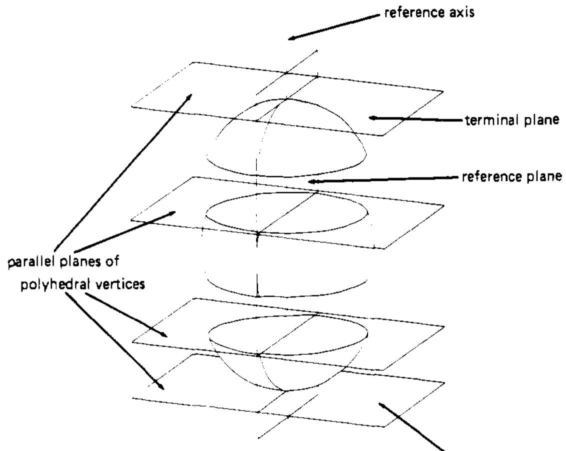

Figure 2. Schematic representation of the features for numbering a polyhedron.

Polyhedra with *capped triangular faces*, except for the trigonal bipyramid, *are not included* in this proposal. Although some of these capped polyhedra can be incorporated directly into the system, others may require additional structural or numbering information in the descriptor in order to be unambiguous. Further, such capped polyhedra may be better described as "derivatives" of noncapped polyhedra in much the same way as bridged organic systems are named.[14b]

Numbering of Closed Polyhedra

For emphasis on the close relationship between the basic principles for numbering polyhedral structures and our proposed structural descriptor, the main numbering principles[4] relating to skeletal characteristics of closed polyboron structures are included here. The principles have not been intentionally changed, but extensions have been proposed to deal with characteristics not previously encountered. To our knowledge, no changes in numbering of known polyboron compounds result from these extensions.

Numbering for the great majority of closed polyboron polyhedra is based mainly on two elements of symmetry, a rotational axis and a symmetry plane. Closed polyboron polyhedra lacking either of these symmetry elements are outside the scope of this summary. The three features necessary for numbering a closed polyboron polyhedron having at least one rotational symmetry axis and at least one symmetry plane are (1) a reference axis, (2) parallel planes containing polyhedral vertices, and (3) a reference plane. These features are identified schematically in Figure 2.

The *reference axis* is a highest order rotational symmetry axis of the polyhedron. Perpendicular to this axis are parallel planes containing *symmetrically equivalent vertices*,[22] rigorously coplanar nonequivalent sets of symmetrically equivalent vertices,[23] or sets of symmetrically equivalent vertices so nearly

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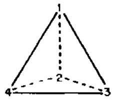
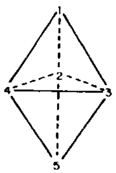
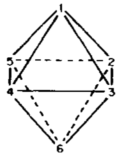
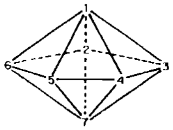
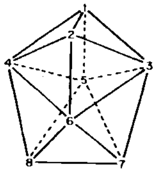
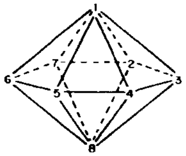
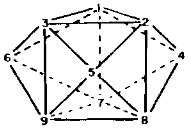
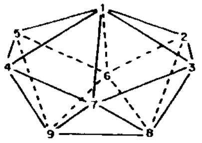
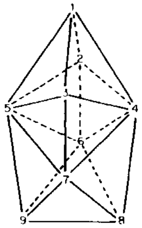
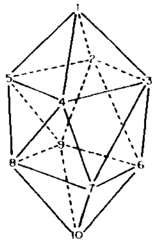
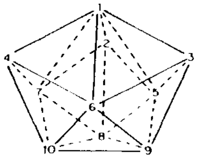
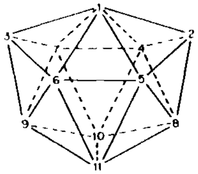
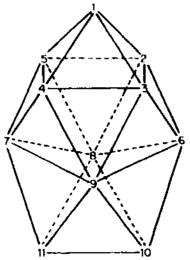
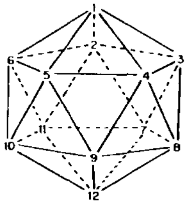
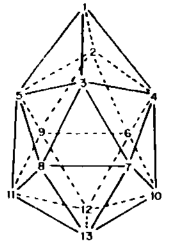
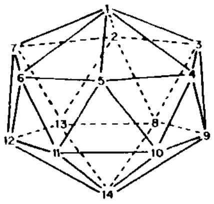
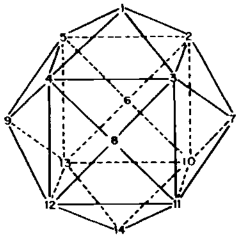
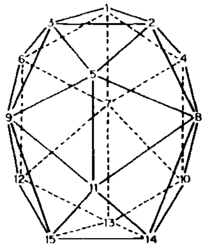
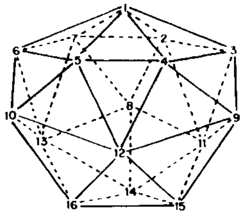
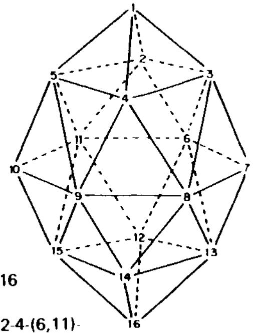
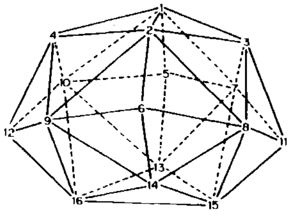
(21) R. M. Adams, private communication.

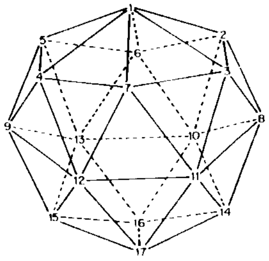
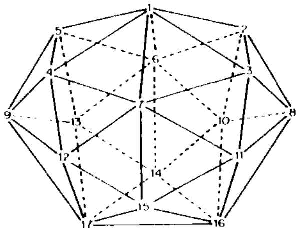
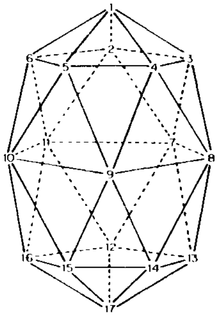
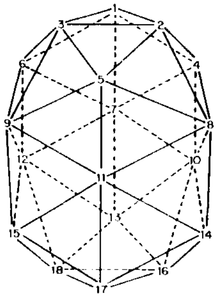
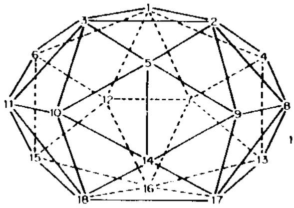
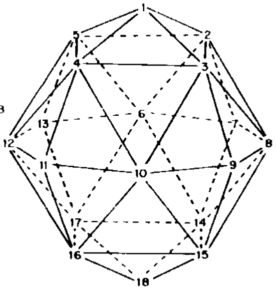
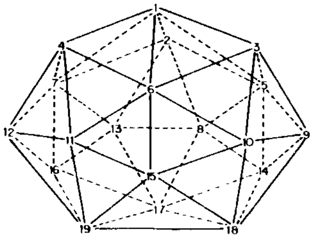
(22) The criterion of symmetrically equivalent vertices is not a part of published rules for numbering closed polyboron structures.[4] However, it is, in fact, what has been done in numbering closed polyhedra, and it has the real advantage of avoiding some uncertainty about coplanarity of polyhedral vertices, which can be troublesome in some of the larger polyhedra.

Table I.[a] Numbering and Proposed Structural Descriptors for Polyboron Polyhedra, $[B_nH_n]^{2-}$ ($n = 4$–24, 32)

	A. $n = 4$	B. $n = 5$	C. $n = 6$	D. $n = 7$	E-1. $n = 8$	E-2. $n = 8$	F-1. $n = 9$	F-2. $n = 9$
Desc.:	[T_d-($1v^33v^3$)-Δ^4-*closo*] [T_d-(13)-Δ^4-*closo*]	[D_{3h}-($1v^33v^41v^3$)-Δ^6-*closo*] [D_{3h}-(131)-Δ^6-*closo*]	[O_h-($1v^44v^41v^4$)-Δ^8-*closo*] [O_h-(141)-Δ^8-*closo*]	[D_{5h}-($15v^41$)-Δ^{10}-*closo*] [D_{5h}-(151)-Δ^{10}-*closo*]	[D_{2d}-($2v^4222v^4$)-Δ^{12}-*closo*] [D_{2d}-(2222)-Δ^{12}-*closo*]	[D_{6h}-($1v^66v^41v^6$)-Δ^{12}-*closo*] [D_{6h}-($1v^661v^6$)-Δ^{12}-*closo*]	[D_{3h}-($33v^43$)-Δ^{14} *closo*] [D_{3h}-(333)-Δ^{14}-*closo*]	[C_{2v}-($1v^64v^422$) Δ^{14}-*closo*]
								
Ref. Axis:	1-(2,3,4)	1-5	1-6	1-7	(1,2)-(7,8)	1-8	(1,2,3)-(7,8,9)	1-(8,9)
Ref. Plane:	1-2-(3,4)	1-2-(3,4,)-5	1-(2,5)-(3,4)-6	1-2-(4,5)-7	1-2-5-6-(7,8)	1-(2,7)-(4,5)-8	1-(2,3)-5-7-(8,9)	1-6-7-(8,9)

	F-3. $n = 9$	G-1. $n = 10$	G-2. $n = 10$	H-1. $n = 11$	H-2. $n = 11$	J. $n = 12$	K. $n = 13$
Desc.:	[C_{2v}-($1v^42v^42v^622v^4$)-Δ^{14}-*closo*]	[D_{4d}-($1v^4441v^4$)-Δ^{16}-*closo*] [D_{4d}-(1441)-Δ^{16}-*closo*]	[C_{3v}-($1v^63v^433$)-Δ^{16}-*closo*]	[C_{2v}-($1v^62v^4422$)-Δ^{18}-*closo*]	[C_{2v}-($1v^4422v^62v^4$)-Δ^{18}-*closo*]	[I_h-(1551) Δ^{20}-*closo*]	[C_{2v}-($1v^422v^6422$)-Δ^{22}-*closo*]
							
Ref. Axis:	1-(8,9)	1-10	1-(8,9,10)	1-(10,11)	1-(10,11)	1-12	1-(12,13)
Ref. Plane:	1-2-3-6-7-(8,9)	1-2-4-(6,9)-(7,8)-10	1-2-6-8-(9,10)	1-(4,7)-(5,6)-10-11	1-(2,5)-(3,4)-8-9-(10,11)	1-2-(4,5)-(7,11)-9-12	1-2-3-(6,9)-(7,8)-12-13

	L-1. $n = 14$	L-2. $n = 14$	M. $n = 15$	N-1. $n = 16$	N-2. $n = 16$	N-3. $n = 16$
Desc.:	[D_{6d}-($1v^6661v^6$)-Δ^{24}-*closo*]	[O_h-($1v^44v^64v^44v^61v^4$)-Δ^{24}-*closo*]	[D_{3h}-($333v^633$)-Δ^{26}-*closo*]	[T_d-($1v^6633v^63$)-Δ^{28}-*closo*]	[D_{2h}-[$1v^4(22v^6)(4v^62v^4)(22v^6)1v^4$]-$\Delta^{28}$-*closo*]	[D_{2d}-($2v^622v^44v^62v^422v^6$)-Δ^{28}-*closo*]
						
Ref. Axis:	1-14	1-14	(1,2,3)-(13,14,15)	1-(14,15,16)	1-16	(1,2)-(15,16)
Ref. Plane:	1-2-5-(8,13)-(10,11)-14	1-(2,5)-(3,4)-6-8-(10,13)-(11,12)-14	1-(2,3)-5-7-11-13-(14,15)	1-(2,7)-(4,5)-8-12-14-(15,16)	1-2-4-(6,11)-(8,9)-12-14-16	1-2-5-6-13-14-(15,16)

	P-1. n **17**	**P-2.** n **17**	**P-3.** n **17**	**Q-1.** n **18**	**Q-2.** n **18**	**Q-3.** n **18**	**R.** n **19**
Desc.:	$[C_{2v}\ (1v^6 4224v^6 22)\ \Delta^{30}\ \mathit{closo}]$	$[C_{2v}\ (1v^6 42v^6 2422v^6)\ \Delta^{30}\ \mathit{closo}]$	$[D_{5h}\ (155v^6 51)\ \Delta^{30}\ \mathit{closo}]$	$[D_{3d}\ (333v^6 3v^6 33)\ \Delta^{32}\ \mathit{closo}]$	$[D_{3h}\ (3v^6 3633v^6)\ \Delta^{32}\text{-}\mathit{closo}]$	$[O_h\ [1v^4 4v^6 (4v^6 4v^4) 4v^6 1v^4]\ \Delta^{32}\text{-}\mathit{closo}]$	$[C_{3v}\text{-}(1v^6 33v^6 633v^6)\ \Delta^{34}\text{-}\mathit{closo}]$
							
Ref. Axis:	1 (16,17)	1 (16,17)	1 17	(1,2,3) (16,17,18)	(1,2,3) (16,17,18)	1 18	1 (17,18,19)
Ref. Plane:	1-6-7-(10,13)-(11,12)-16-17	1 6 7 14 15 (16,17)	1 2 (4,5) (7,11) 9 12 (14,15) 17	1 (2,3) 5,7 11 13 (16,18) 17	1 (2,3) 5-(7,12) 14-16-(17,18)	1 (2,5) (3,4) 6 10-(14,17)-(15,16) 18	1 2-6-(8,13) 15-17 (18,19)

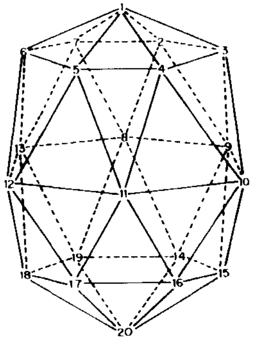
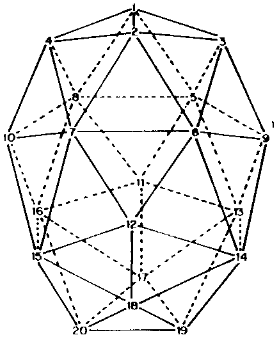
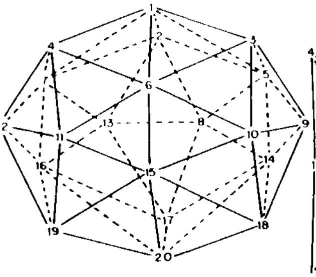
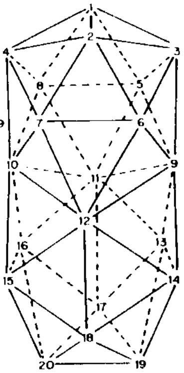
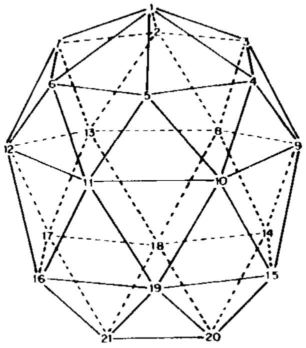
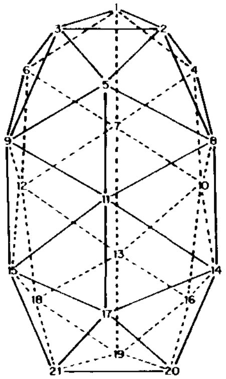
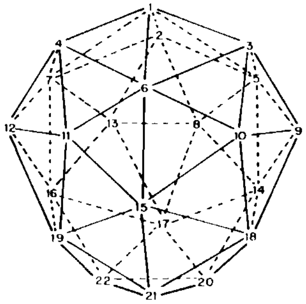
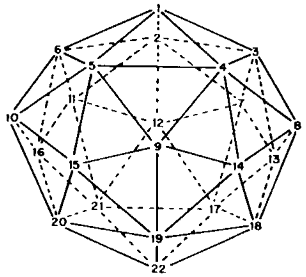
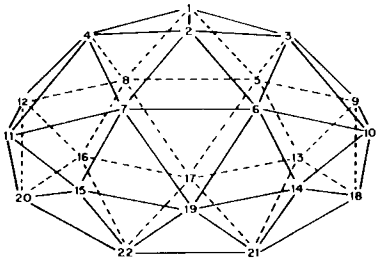
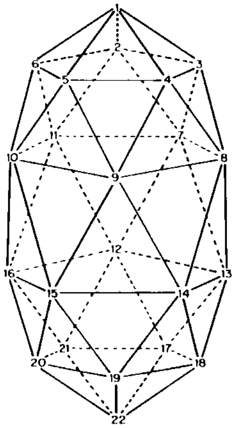
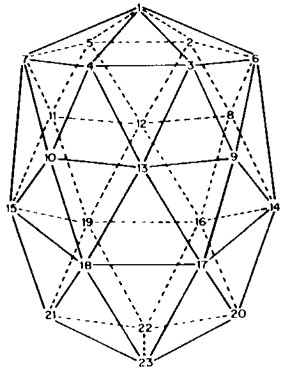
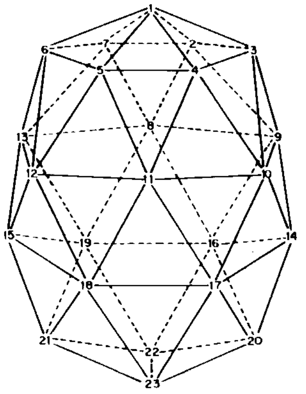
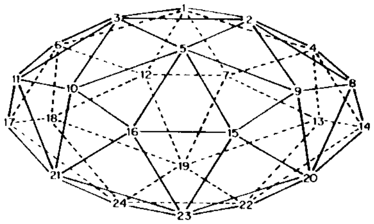
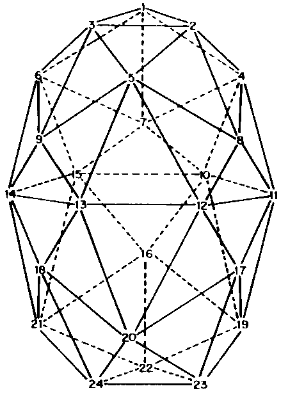
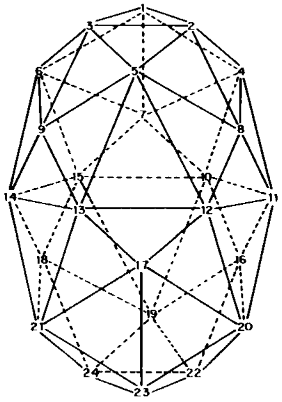
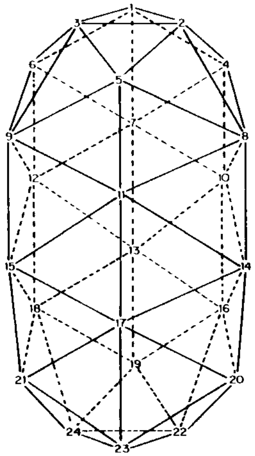
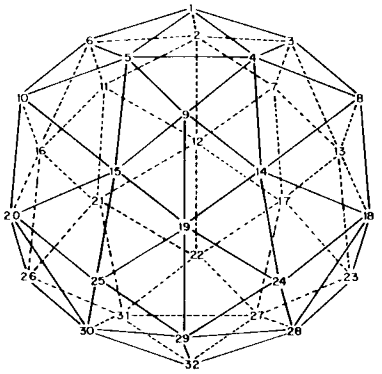
	S-1. n **20**	**S-2.** n **20**	**S-3.** n **20**	**S-4.** n **20**	**T-1.** n **21**	**T-2.** n **21**	**U-1.** n **22**
Desc.:	$[D_{6h}\text{-}(1v^6 66v^6 61v^6)\text{-}\Delta^{36}\text{-}\mathit{closo}]$	$[D_{2d}\text{-}(224v^6 224v^6 22)\ \Delta^{36}\ \mathit{closo}]$	$[D_{3h}\text{-}(1v^6 33v^6 63v^6 31v^6)\text{-}\Delta^{36}\ \mathit{closo}]$	$[D_{2d}\text{-}(2242v^7 2v^7 422)\text{-}\Delta^{36}\ \mathit{closo}]$	$[C_{2v}\ (1v^6 [6] [6v^6] 42v^6 2)\text{-}\Delta^{38}\text{-}\mathit{closo}]$	$[D_{3h}\text{-}(333v^6 3v^6 3v^6 33)\ \Delta^{38}\text{-}\mathit{closo}]$	$[T_d\text{-}(1v^6 33v^6 63v^6 3v^6 3)\text{-}\Delta^{40}\text{-}\mathit{closo}]$
							
Ref. Axis:	1 20	(1,2)-(19,20)	1-20	(1,2) (19,20)	1 (20,21)	(1,2,3)-(19,20,21)	1-(20,21,22)
Ref. Plane:	1-(2,7) (4,5)-8-11 (14,19)- (16,17)-20	1-2-(5.8)-(6,7)-11- 12-17-18-(19,20)	1-2-6-(8.13) 15-17-20	1-2 (5.8)-(6.7) 11-12-17-18-(19,20)	1-2-5 (8,13)-(10,11)-18-19-(20,21)	1-(2,3)-5-7 11 13 17 19-(20.21)	1-2-6-(8,13)-15-17-(20,22)-21

Table I (*Continued*)

	U-2. $n = 22$	U-3. $n = 22$	U-4. $n = 22$	V-1. $n = 23$	V-2. $n = 23$
Desc.:	$[D_{5d}\text{-}(15\upsilon^{6}555\upsilon^{6}1)\text{-}\Delta^{40}\text{-}\mathit{closo}]$	$[C_{2v}\text{-}(22\upsilon^{6}4\upsilon^{6}44[2\upsilon^{6}2]2\upsilon^{6})\text{-}\Delta^{40}\text{-}\mathit{closo}]$	$[D_{5d}\text{-}(155\upsilon^{6}5\upsilon^{6}51)\text{-}\Delta^{40}\text{-}\mathit{closo}]$	$[C_{2v}\text{-}(1\upsilon^{6}42\upsilon^{6}42\upsilon^{6}2\upsilon^{6}4\upsilon^{6}22)\text{-}\Delta^{42}\text{-}\mathit{closo}]$	$[C_{2v}\text{-}(1\upsilon^{6}[6][6\upsilon^{6}]24\upsilon^{6}22)\text{-}\Delta^{42}\text{-}\mathit{closo}]$
					
Ref. Axis:	1-22	(1,2)-(21,22)	1-22	1-(22,23)	1-(22,23)
Ref. Plane:	1-2-(4,5)-9-12-(17,21)-19-22	1-2-(5,8)-(6,7)-17-19-(21,22)	1-2-(4,5)-(7,11)-9-12-(14,15)-(17,21)-19-22	1-(2,5)-(3,4)-12-13-(16,19)-(17,18)-22-23	1-(2,7)-(4,5)-8-11-(16,19)-(17,18)-22-23

	W-1. $n = 24$	W-2. $n = 24$	W-3. $n = 24$	W-4. $n = 24$	X. $n = 32$
Desc.:	$[D_{3d}\text{-}(3\upsilon^{6}3\upsilon^{6}663\upsilon^{6}3\upsilon^{6})\text{-}\Delta^{44}\text{-}\mathit{closo}]$	$[D_{3h}\text{-}(33\upsilon^{6}36\upsilon^{6}33\upsilon^{6}3)\text{-}\Delta^{44}\text{-}\mathit{closo}]$	$[D_{3d}\text{-}(33\upsilon^{6}36\upsilon^{6}33\upsilon^{6}3)\text{-}\Delta^{44}\text{-}\mathit{closo}]$	$[D_{3d}\text{-}(333\upsilon^{6}3\upsilon^{6}3\upsilon^{6}3\upsilon^{6}33)\text{-}\Delta^{44}\text{-}\mathit{closo}]$	$[I_{h}\text{-}(15\upsilon^{6}55\upsilon^{6}5\upsilon^{6}55\upsilon^{6}1)\text{-}\Delta^{60}\text{-}\mathit{closo}]$
					
Ref. Axis:	(1,2,3)-(22,23,24)	(1,2,3)-(22,23,24)	(1,2,3)-(22,23,24)	(1,2,3)-(22,23,24)	1-32
Ref. Plane:	1-(2,3)-5-(7,12)-(15,16)-19-(22,24)-23	1-(2,3)-5-7-(10,15)-(12,13)-16-20-22-(23,24)	1-(2,3)-5-7-(10,15)-(12,13)-17-19-(22,24)-23	1-(2,3)-5-7-11-13-17-19-(22,24)-23	1-2-(4,5)-9-12-19-22-(27,31)-29-32

coplanar that it is virtually impossible to select one set to cite and number first.[23] Planes of polyhedral vertices furthest from the centroid of the polyhedron are called terminal planes. The *reference plane* is a symmetry plane of the polyhedron and must include the reference axis.

The principles for numbering the closed polyhedral frameworks shown in Table I are given below. Further choices for assigning locants to polyhedral vertices should follow accepted principles from other nomenclature systems but are not within the scope of this report.

1. Select the *reference axis*, i.e., a rotational symmetry axis of highest order that lies in a symmetry plane of the polyhedron.[24]

This criterion has been sufficient for choosing the reference axis of all known closed polyboron structures having at least one rotational symmetry axis and one symmetry plane. However, it alone does not allow a reference axis to be chosen in a D_{2h} polyhedron (see Figure 4 and discussion later). Hence, we suggest that, when a further choice is needed for selecting a reference axis, the following criteria be applied in sequence: (a) The reference axis should have a terminal plane with the fewest number of polyhedral vertices. (b) The reference axis should lie in the reference plane (see principle 3, below).

2. Select the *preferred terminal plane* of symmetrically equivalent vertices, which defines the *preferred end* of the *reference axis*. The preferred terminal plane (a) contains the fewer number of polyhedral vertices and, if these are the same, (b) has the vertices with the fewer total number of skeletal connectivities.

If a further choice is needed, the preferred terminal plane is nearer to the parallel plane of symmetrically equivalent vertices preferred by applying criteria 2(a) and 2(b), above, successively to pairs of parallel planes proceeding inward from each terminal plane.

3. Select the *reference plane*, i.e., a symmetry plane of the polyhedron that contains the reference axis.

If there is more than one symmetry plane containing the reference axis, or if a selection of a reference axis was not effected by principle 1, the reference plane is chosen by application of the following criteria, sequentially, until a decision is made: (a) The reference plane passes through the least number of polyhedral vertices; a symmetry plane that does not pass through any vertex is preferred. (b) The reference plane passes through a polyhedral vertex in a plane of symmetrically equivalent vertices that is nearer to the preferred terminal plane (see principle 2, above); i.e., polyhedral vertices in the reference plane have the lower locant numbers when assigned according to principles 4 and 5, below. (c) The reference plane passes through a polyhedral vertex with the fewest number of associated polyhedral edges; i.e., polyhedral vertices with the lowest skeletal connectivity in the reference plane have the lower locant numbers when assigned according to principles 4 and 5, below.

4. *Orient the polyhedron*, in order to provide a consistent reference point for numbering, by looking down the reference axis from the preferred end (see principle 2, above) and rotating the polyhedron until the reference plane (see principle 3, above) is vertical. If a choice is needed, the preferred orientation has a polyhedral vertex of the preferred terminal plane, or in a parallel plane nearest to it, at the top of the orientation in the reference plane.

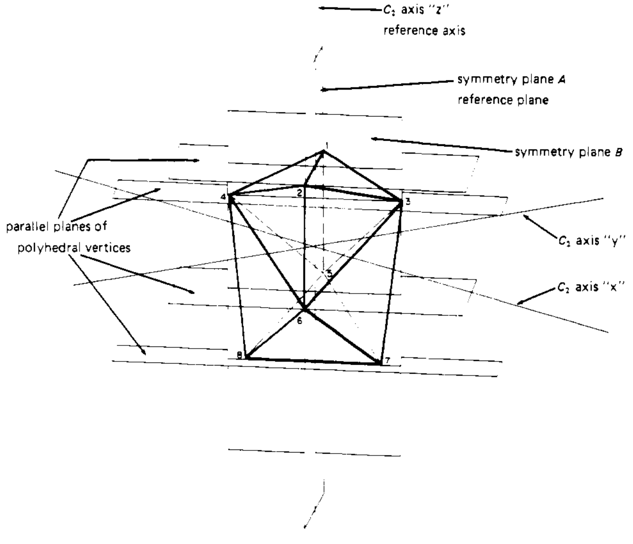


Figure 3. D_{2d} 8-vertex dodecahedron.

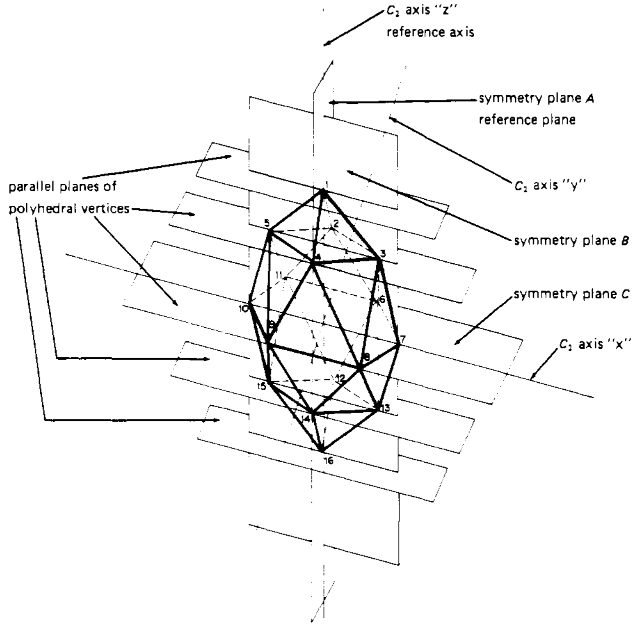


Figure 4. D_{2h} 16-vertex octacosahedron.

5. *Number the vertices* of the polyhedron consecutively, clockwise or anticlockwise, starting with vertices in the preferred terminal plane and proceeding successively to succeeding planes of vertices, working down the reference axis from the preferred end. The vertices in each plane are numbered in the same direction as the preceding and/or following planes, beginning in each plane with a vertex at the top of the preferred orientation (see principle 4, above), or with the first vertex encountered, in the direction chosen for numbering, from the top of the preferred orientation.

Most of these principles are illustrated by the two polyhedra shown in Figures 3 and 4.

The familiar D_{2d} dodecahedron shown in Figure 3 (structure

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(23) These situations are illustrated by structures N-2, Q-3, T-1, U-3, and V-2 and are indicated in the descriptor by enclosing the rigorously coplanar nonequivalent sets of symmetrically equivalent vertices in parentheses and the nearly coplanar symmetrically equivalent sets in brackets. In such cases, it seems to be more convenient to number these polyhedral vertices sequentially rather than discontinuously. In each case, the first set cited in the descriptor is the one where the numbering begins in that plane.

(24) The published rules for numbering closed polyboron structures[4] require the reference axis to be the "longest highest-order" rotational symmetry axis but do not define "longest". To our knowledge, the criterion of "longest" has not yet been needed for numbering closed polyhedral frameworks. Since we did not find a need for this criterion and it might not be easy to define "longest", we have not included it in this summary of numbering rules.

E-1 in Table I) has three C_2 axes: "x", passing through edges 3–6 and 4–5; "y", passing through edges 3–5 and 4–6; and "z", passing through edges 1–2 and 7–8. It also has two symmetry planes: A, passing through vertices 1, 2, 5, and 6; and B, passing through vertices 3, 4, 7, and 8. In this polyhedron, only the "z" C_2 axis can be the reference axis since it is the only C_2 axis lying in a symmetry plane of the polyhedron. The two symmetry planes of this polyhedron are equivalent in that both contain the reference axis (the "z" C_2 axis), and both pass through four polyhedral vertices. Symmetry plane A is shown as the reference plane in Figure 3, because in the preferred orientation it passes through the polyhedral vertices of a terminal plane.

The D_{2d} polyhedron in Figure 3 is oriented for numbering by looking down the "z" C_2 axis, in this case from either end, and rotating the structure until one of the symmetry planes containing the vertices in a terminal plane is vertical. For this structure, this symmetry plane is the reference plane. The vertex at the top of the reference plane is assigned the locant number 1, and the vertex at the bottom, the locant number 2. The two vertices in the next plane of vertices perpendicular to the "z" C_2 axis are assigned locant numbers 3 and 4,[25] and the vertices in the third and fourth perpendicular planes are assigned the locant numbers 5, 6 and 7, 8, in the same way as for the first two planes.

The D_{2h} 16-vertex polyhedron shown in Figure 4 (structure N-2 in Table I) also has three C_2 axes: "x", passing through vertices 7 and 10; "y", passing through edges 6–11 and 8–9; and "z", passing through vertices 1 and 16. It has three symmetry planes: A, passing through vertices 1, 2, 4, 12, 14, and 16; B, passing through vertices 1, 3, 5, 7, 10, 13, 15, and 16; and C, passing through vertices 6, 7, 8, 9, 10, and 11. Each C_2 axis in this polyhedron is contained in two symmetry planes: the "x" C_2 axis in symmetry planes B and C; the "y" C_2 axis in A and C; and the "z" C_2 axis in A and B. Therefore, for this polyhedron, it is necessary to consider the additional criteria of principle 1 in order to select the reference axis.

Since the terminal plane perpendicular to the "y" C_2 axis contains two polyhedral vertices, according to principle 1a it is less preferred than the "x" or "z" C_2 axis, each of which has a perpendicular terminal plane with only one polyhedral vertex. The next criterion for selecting the reference axis under principle 1 involves selection of the reference plane (see principle 3). Since symmetry plane B passes through eight polyhedral vertices, according to principle 3a, above, it is less preferred than symmetry planes A or C, each of which passes through six vertices. Symmetry plane A passes through a vertex in the second plane of vertices perpendicular to the "z" C_2 axis, but symmetry plane C does not pass through a vertex until the third plane of vertices perpendicular to the "x" C_2 axis. Therefore, according to principle 3b, symmetry plane A is the reference plane, and since the "z" C_2 axis lies in the reference plane, it is the reference axis.

The D_{2h} polyhedron in Figure 4 also illustrates the type of structure with rigorously coplanar nonequivalent sets of symmetrically equivalent vertices. As noted earlier, it seems more convenient to number the vertices in each such plane sequentially rather than discontinuously. Hence, after the locant number 1 is assigned to the polyhedral vertex in the preferred terminal plane, the locant numbers 2, 3, 4, and 5 are assigned sequentially, clockwise or anticlockwise,[25] to the vertices in the next plane starting with the v^5 vertex at the top of the projection in the reference plane. In the same way, locant numbers 6, 7, 8, 9, 10, and 11 are assigned to the vertices in the third plane in the same direction from the reference plane as the numbering was done in the second plane beginning with the v^6 vertex nearest to the top of the projection.

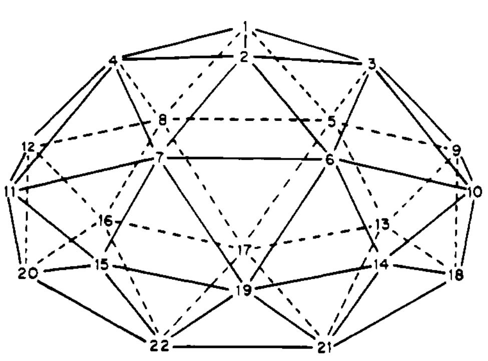

Figure 5. C_{2v} 22-vertex tetracontahedron.

In the descriptor for this polyhedron, [D_{2h}-[1v^4(22v^6)-(4$v^6$2v^4)(22v^6)1v^4]-Δ^{28}-*closo*], the notations for the polyhedral vertices in the three nonterminal planes are enclosed in parentheses and cited in the order of increasing initial locant numbers. Thus, since a v^5 vertex in the second plane is assigned locant number 2, the v^5 vertices are cited first in the descriptor. Similarly, since a v^6 vertex in the third plane is assigned locant number 6, the v^6 vertices are cited first.

Occasionally, polyhedra may be encountered where sets of symmetrically equivalent vertices are not coplanar but are close enough to each other to make it quite difficult, perhaps impossible, even in an idealized model, to determine which coplanar sets of vertices to identify and number first. This situation tends to be more prevalent in larger polyhedra. One such polyhedron is shown in Figure 5 (structure U-3 in Table I). In our model of this polyhedron, it is reasonably clear that the symmetrically equivalent vertices 13, 14, 15, and 16 are above vertices 17, 18, 19, and 20. However, it is equally uncertain which of the two nonequivalent sets of symmetrically equivalent vertices, 17 and 19, or 18 and 20, occurs next in the sequence of parallel planes and should be numbered and cited next. It seems quite reasonable that such sets should not be treated exactly as the rigorously coplanar nonequivalent sets, illustrated by the polyhedral structures N-2 and Q-3 in Table I. However, it also seems quite reasonable and convenient to number such nearly coplanar nonequivalent sets sequentially. Therefore, when it is difficult, or virtually impossible to separate sets of symmetrically equivalent vertices into individual planes, we suggest that these sets be enclosed in brackets, instead of parentheses, but be numbered and cited in the descriptor in the same way as for the rigorously coplanar nonequivalent sets. Thus, the descriptor for the 22-vertex tetracontahedron in Figure 5 (structure U-3 in Table I) is [C_{2v}-(22$v^6$4$v^6$44[2$v^6$2]2v^6)-Δ^{40}-*closo*].

Structures T-1 and V-2 in Table I are further examples of polyhedra with nearly coplanar sets of symmetrically equivalent vertices. However, in these structures, the nearly coplanar sets have vertices with the same skeletal connectivity. The vertices are numbered sequentially, and the v^n symbol is enclosed in brackets in the descriptor since they are not rigorously coplanar.

We would emphasize, however, that the technique sugested for the structure of Figure 5 should be used only when there is real uncertainty regarding the position of planes of symmetrically equivalent vertices. It should not be a substitute for the rigorous system.

Summary

A method for uniquely describing the structure of closed polyhedral systems, with at least one rotational symmetry axis and one plane of symmetry, has been developed that is con-

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(25) Although the locant number 3 may be assigned either to the right or to the left of the reference plane in accordance with a clockwise or anticlockwise direction, respectively, it is customary to use a clockwise direction in the absence of specific atoms and substituents or ligands at the vertices of the polyhedron.

sistent with present procedures for numbering coordination polyhedra and boron polyhedral frameworks. Comments on this proposal are encouraged.

Polyhedral structures belonging to D_n, T, and C_s symmetry point groups, capped polyhedral systems, encapsulating polyhedra, and extensions specific to metal clusters are not included in this paper, but proposals in this area are in preparation.

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A Designed Metallacarborane Catalyst. Synthesis, Structure, and Reactions of [*closo*-1,3-[μ-(η^2-3-CH_2=$CHCH_2CH_2$)]-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$]

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The synthesis and reactions of a designed metallacarborane catalyst, [*closo*-1,3-[μ-(η^2-3-CH_2=$CHCH_2CH_2$)-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$] (I), are reported. Complex I contains a chelating 4-butenyl side chain attached to the dicarbollide ligand, the alkenyl function of which formally replaces one of the triphenylphosphine ligands of the parent compound [*closo*-3-H-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$] (II). When I was exposed to conditions employed for the hydrogenation of alkenes or alkynes, the alkenyl ligand was hydrogenated to a noncoordinating butyl group, leaving an open coordination site on rhodium which greatly enhanced the rate of hydrogenation of added alkene. Complex I was, indeed, found to be among the most active homogeneous hydrogenation catalysts reported. Complex I also catalyzed the isomerization of hex-1-ene. The crystal and molecular structure of I has been determined by three-dimensional X-ray diffraction techniques. The compound crystallizes in the monoclinic space group $P2_1/a$ with a = 16.494 (4) Å, b = 11.193 (2) Å, c = 17.006 (3) Å, β = 122.49 (1)°, and Z = 4. The observed and calculated densities are 1.229 and 1.386 g cm^{-3}, respectively. Diffraction data to 2θ maximum = 45° (Mo Kα radiation) were collected on a Syntex P$\bar{1}$ automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares techniques to a final discrepancy index of R = 0.044 for the 2253 independent observed reflections. All atoms, including hydrogen atoms, were located. The molecule has the closo 12-vertex icosahedral geometry, and the rhodium is bonded to one hydrogen atom and one triphenylphosphine ligand and π bonded to the alkene function as well as symmetrically bonded to the C_2B_3 face of the C_2B_9 dicarbollyl group. The molecule is monomeric, and there are no intermolecular distances shorter than van der Waals distances. The reactions of I with hydrogen in the presence and absence of triphenylphosphine are reported.

Introduction

During the course of our studies of alkene hydrogenations catalyzed by [*closo*-3-H-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$] (II),[1] the first metallacarborane catalyst, we have noted that the rate of hydrogenation is inversely proportional to the concentration of added triphenylphosphine. This observation suggests that reversible dissociation of triphenylphosphine is an important equilibrium preceding the rate-determining step of the hydrogenation sequence. The ease with which the parent catalyst could be modified through synthesis led us to explore the possibility of obtaining enhanced hydrogenation rates by replacing one of the triphenylphosphine ligands with a chelated η^2-3-buten-1-yl side chain attached to one of the dicarbollide carbon atoms. The resulting rhodacarborane [*closo*-1,3-[μ-(η^2-3-CH_2=$CHCH_2CH_2$)]-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$][2] (I) might well undergo irreversible hydrogenation of the alkenyl side chain to produce an open coordination site on rhodium and a noncoordinating butyl group attached to the dicarbollide ligand. The use of alkenyl ligands to produce an open coordination site in hydrogenation catalysts was first proposed by Schrock and Osborn in their studies of hydrogenations catalyzed by $[(COD)MCl]_2$ (COD = 1,5-cyclooctadiene, M = Rh, Ir)[3]. To our knowledge, I is the first rhodium member of the relatively rare hydrido alkene class of complexes[4-12] to be isolated and structurally characterized. Regardless of the detailed mechanism of rhodacarborane-catalyzed hydrogenation (a subject which will be reported elsewhere), the removal of one coordinated triphenylphosphine molecule from the manifold of available ligands should facilitate alkene or hydrogen coordination and lead to a marked rate acceleration. Preliminary catalytic screening of I conclusively demonstrated this effect; indeed I is among the most active homogeneous hydrogenation catalysts reported to date (vide infra).

Experimental Section

Solvents and Reagents. All solvents were reagent grade and distilled under argon prior to use. Tetrahydrofuran (THF) was dried over

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