

Chemical Applications of Topology and Group Theory. V. Polyhedral Metal Clusters and Boron Hydrides¹

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Abstract: Possible polyhedra and polyhedral fragments for clusters of up to 12 atoms are generated by considering the following systems: (1) closed triangulated polyhedra and (2) open triangulated polyhedral fragments with numbers of vertices (v), edges (e), (triangular) faces (t), and connectivities (h) satisfying the relationships $v + t - e = 3 - h$ (generalized Euler's relationship), $2e \geq 3t$, $t \geq v - 2$, and $2h \leq 2v - t - 2$. The polyhedra so generated are compared with those actually found in transition metal clusters and in polyhedral boron hydrides. Transition metal clusters avoid using polyhedra with any vertices of order five or higher, because this would lead either to excessive angular strain or a very high coordination number. Closed boron hydride and carborane cages utilize when possible polyhedra with all vertices of orders four and five. Vertices of orders three and six are avoided as much as possible in the polyhedral boron hydride and carborane cages.

Two classes of compounds that have received much attention in recent years are metal cluster compounds³⁻⁵ and boron hydride cages.^{6,7} This paper examines possible metal⁸ polyhedra and polyhedral fragments for this class of compounds using mathematical techniques similar to those used in the first paper of this series⁹ for the examination of coordination polyhedra. However, in the polyhedra discussed in the present paper, the vertices and edges correspond to metal atoms and metal-metal bonds, respectively, whereas, in the polyhedra discussed in earlier papers^{1,9,10} the vertices and edges correspond to ligand atoms and metal-ligand bonds, respectively.

Generation of Possible Polyhedra and Polyhedral Fragments

A metal cluster is defined as a network of metal atoms held together by metal-metal bonds with at least two metal-metal bonds to each metal atom. In any such metal cluster, each metal atom is part of some ring of metal atoms. This definition excludes from consideration acyclic metal chains, since not only are the metal atoms not parts of rings but also the end metal atoms of a metal chain have only one metal-metal bond. This definition of a metal cluster allows each metal cluster to be represented as a polyhedron or a polyhedral fragment with the vertices corresponding to metal atoms, the edges corresponding to metal-metal bonds, and the faces "real" polygons with at least three sides (edges). In such polyhedral models for metal clusters all ligands, even bridging ones, are ignored. If, after removing from consideration all metal-ligand bonds,

the remaining network of metal-metal bonds is insufficient to hold the entire group of metal atoms together, the resulting system is better considered as the combination of the resulting separate smaller metal clusters, metal chains, and/or isolated metal atoms.

A network of metal atoms can be considered as a group of line segments (metal chains), triangles (metal clusters), quadrilaterals (metal clusters), pentagons (metal clusters), etc., or any combination of these basic building blocks. In the case of transition metal derivatives (not boron hydrides, however), the edges of the network correspond to metal-metal bonds with each such metal-metal bond containing two bonding electrons. Table I summarizes the total number of bond-

Table I. Comparison of Different Arrangements of Atoms

| Arrangement | No. of atoms | Max interatomic dist ^a | No. of bonding electrons | Bonding electrons per atom |
|-------------|--------------|-----------------------------------|--------------------------|----------------------------|
| Linear | 2 | 1.00 | 2 | 1 |
| Triangle | 3 | 1.00 | 6 | 2 |
| Square | 4 | 1.41 | 8 | 2 |

^a Here the bond length is taken as the unit of length.

ing electrons and the number of bonding electrons per metal atom for three basic building blocks of metal networks: the line segment, the triangle, and the square. The closed polygons (triangle and square) possess twice the number of bonding electrons per metal atom as compared with the line segment.

The simplest metal cluster contains a triangle of metal atoms. An equivalent orbital description of the metal triangle¹¹ as found in $\text{Re}_3\text{Cl}_{12}^{3-}$ indicates further delocalization involving interactions between the three rhenium-rhenium bonds; such delocalization would be expected to decrease rapidly with increasing distances between the metal-metal bonds. Table I summarizes the maximum distances between pairs of metal atoms for the same three basic building blocks for metal networks discussed above. The smallest maximum metal atom pair distances are found for the line segment and the triangle; this distance increases monotonically as

(1) For part IV of this series see R. B. King, *J. Amer. Chem. Soc.*, **92**, 6460 (1970).

(2) Fellow of the Alfred P. Sloan Foundation, 1967-1969.

(3) F. A. Cotton, *Quart. Rev., Chem. Soc.*, **20**, 389 (1966).

(4) M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968).

(5) The author has done a detailed survey of the literature on metal cluster compounds, including more recent papers than those covered by ref 3 and 4. A review article covering this literature on metal cluster compounds will appear in *Progr. Inorg. Chem.*, in press.

(6) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(7) E. L. Muetterties and W. H. Knoch, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968.

(8) For brevity, the term "metal" in the general discussion includes boron unless otherwise specified.

(9) R. B. King, *J. Amer. Chem. Soc.*, **91**, 7211 (1969).

(10) R. B. King, *ibid.*, **92**, 6455 (1970).

(11) S. F. A. Kettle, *Theor. Chim. Acta*, **3**, 282 (1965).

Table II. Closed Triangulated Polyhedra

| Polyhedron ^a | Point group | No. of elements ^a | | | | Types of vertices ^a | | | |
|---|------------------------|------------------------------|----------|----------|------------|--|-----------------------|-----------------------|-----------------------|
| | | <i>v</i> | <i>e</i> | <i>t</i> | <i>e/v</i> | <i>j</i> ₃ | <i>j</i> ₄ | <i>j</i> ₅ | <i>j</i> ₆ |
| Planar triangle | <i>D</i> _{3h} | 3 | 3 | 2 | 1.00 | <i>j</i> ₂ = 3, <i>j</i> ₃ = <i>j</i> ₄ = <i>j</i> ₅ = <i>j</i> ₆ = 0 | | | |
| Tetrahedron | <i>T</i> _d | 4 | 6 | 4 | 1.50 | 4 | 0 | 0 | 0 |
| Trigonal bipyramid | <i>D</i> _{3h} | 5 | 9 | 6 | 1.80 | 2 | 3 | 0 | 0 |
| Octahedron | <i>O</i> _h | 6 | 12 | 8 | 2.00 | 0 | 6 | 0 | 0 |
| Pentagonal bipyramid | <i>D</i> _{5h} | 7 | 15 | 10 | 2.14 | 0 | 5 | 2 | 0 |
| Capped octahedron | <i>C</i> _{3v} | 7 | 15 | 10 | 2.14 | 1 | 3 | 3 | 0 |
| Bicapped octahedron | <i>D</i> _{3d} | 8 | 18 | 12 | 2.25 | 2 | 0 | 6 | 0 |
| "Dodecahedron" | <i>D</i> _{2d} | 8 | 18 | 12 | 2.25 | 0 | 4 | 4 | 0 |
| 4,4,4-Tricapped trigonal prism | <i>D</i> _{3h} | 9 | 21 | 14 | 2.33 | 0 | 3 | 6 | 0 |
| Staggered 252 stack ^c | <i>C</i> _{2v} | 9 | 21 | 14 | 2.33 | 0 | 5 | 2 | 2 |
| 4,4-Bicapped square antiprism | <i>D</i> _{4d} | 10 | 24 | 16 | 2.40 | 0 | 2 | 8 | 0 |
| 3,4,4,4-Tetracapped trigonal prism | <i>C</i> _{3v} | 10 | 24 | 16 | 2.40 | 1 | 3 | 3 | 3 |
| Pentacapped trigonal prism | <i>D</i> _{3h} | 11 | 27 | 18 | 2.45 | 2 | 3 | 0 | 6 |
| B ₁₁ H ₁₁ ²⁻ polyhedron ^b | <i>C</i> _{2v} | 11 | 27 | 18 | 2.45 | 0 | 2 | 8 | 1 |
| Icosahedron | <i>I</i> _h | 12 | 30 | 20 | 2.50 | 0 | 0 | 12 | 0 |

^a The terminology and symbols used in this table are defined by R. B. King, *J. Amer. Chem. Soc.*, **91**, 7211 (1969). ^b For a picture of this polyhedron, see Figure 5 of F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966). ^c See Table I of R. B. King, *J. Amer. Chem. Soc.*, **92**, 6460 (1970).

the number of sides of the metal polygon is increased.

The metal triangle is thus indicated to be the most favorable unit to build more complex metal clusters for the following reasons: (1) maximization of the number of bonding electrons per metal atom; (2) among the possible planar polygonal units with the maximum number of bonding electrons per metal atom, the metal triangle has the smallest maximum intermetallic distance, thereby maximizing interactions between the metal-metal bonds.¹² Triangles of boron atoms are likewise the most favorable building blocks for polyhedral boron hydrides since such triangles maximize overlap in the boron-boron-boron three-center bonding characteristic of polynuclear boron hydrides.¹² All of these considerations suggest that the possible polyhedral networks for both metal clusters and boron hydrides can be generated by consideration of possible ways of joining triangles into polyhedral networks with each triangle having at least one side in common with some other triangle of the network in order to allow cross-delocalization through mechanisms similar to that for a single triangular face¹¹ but involving bonds and atoms in different triangular faces. Such a triangulated⁹ polyhedral metal network represents the range of possible delocalization in a metal cluster or boron hydride in a manner similar to the planar network of fused hexagons and related polygons in a polycyclic aromatic system. The treatment used in this paper assumes that delocalization¹¹ is significant only in triangular faces and is negligible in square, pentagonal, and higher *n*-gonal faces. The square, pentagonal, and higher *n*-gonal faces are thus regarded as "insulators" similar to methylene groups and other sp³ carbons in joined aromatic systems. For this reason, only polyhedra and polyhedral fragments with only triangular faces ("triangulated polyhedra")⁹ are allowed; faces with more than three edges are regarded as holes, since such insulating faces interrupt the delocalization.

Two types of triangulated polyhedral networks are relevant to the chemistry of metal clusters and polyhedral boron hydrides. The first type comprises the closed triangulated⁹ polyhedra similar to the triangulated coordination polyhedra discussed in previous pa-

(12) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 117 (1959).

pers.^{1,9} The closo¹³ polyhedral boranes have the boron atoms at the vertices of such polyhedra. Table II lists the possible closed triangulated polyhedra with up to 12 vertices. Two isogonal¹⁴ triangulated polyhedra with principal rotation axes of different and mutually prime orders are listed for seven-, eight-, nine-, and ten-atom systems, since in each of these systems both of the listed isogonal polyhedra must initially be considered as candidates for metal clusters. Two isogonal polyhedra are also listed for the 11-atom system, but here the less symmetrical *C*_{2v} 11,27,18 (B₁₁H₁₁²⁻) polyhedron may be regarded as derived from the *D*_{3h} pentacapped trigonal prism by distortion to remove the threefold rotation axis and to change the connected vertices such that all but one of the vertices of order six are removed.

The second type of triangulated polyhedral network comprises open triangulated polyhedral fragments such as those found in the nido¹³ polyboranes. In an open polyhedral network, it is possible without going through a face to go from the outside to the inside or *vice versa* by going through a hole in the network or by the topologically equivalent process of going off the end of the network and coming back on the other side. Possible open triangulated polyhedral fragments may be generated by a procedure conceptually similar to that used for the closed coordination polyhedra^{1,9} but differing significantly in detail. In addition to the parameters *v*, *e*, *f*, *t*, *q*, and *j*_{*i*}, and others⁹ used to describe characteristic features of closed polyhedra, the following additional parameters are needed to describe the characteristics of holes in open triangulated polyhedral fragments: *h*, the connectivity of the fragment as defined in the conventional topological manner¹⁵ (the relationship *H* = *h* - 1 holds where *H* represents the number of holes; all closed polyhedra have unit connectivity); *z*_{*n*}, the number of edges bordering a given hole *n* (thus for a quadrilateral hole, *z*₄ = 4); *Z*, the total number of edges bordering holes. The first paper of this series⁹

(13) R. Adams, *Inorg. Chem.*, **2**, 1087 (1963); nomenclature of the Council of the American Chemical Society *ibid.*, **7**, 1945 (1968).

(14) In this paper two closed polyhedra with the same number of vertices are said to be "isogonal" if they have the same number of edges (and hence, by Euler's relationship, also the same number of sides). Isogonal polyhedra thus have the same *v*, *e*, and *f* values.

(15) D. Hilbert and S. Cohn-Vossen, "Geometry and the Imagination," Chelsea, New York, N. Y., 1952, pp 289-295.

Table III. Open Triangulated Polyhedral Networks^a

| Structure ^b | Point group ^c | No. of elements ^d | | | | Types of vertices ^d | | | | <i>h</i> ^e | <i>z</i> ^e | Remarks ^f |
|------------------------|--------------------------|------------------------------|----------|----------|------------|--------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|---|
| | | <i>v</i> | <i>e</i> | <i>t</i> | <i>e/v</i> | <i>j</i> ₂ | <i>j</i> ₃ | <i>j</i> ₄ | <i>j</i> ₅ | | | |
| 1 | <i>C</i> _{2v} | 4 | 5 | 2 | 1.25 | 2 | 2 | 0 | 0 | 2 | 4 | (A) 4-Atom System "Butterfly shape," Co ₄ (CO) ₁₀ C ₂ R ₂ , Re ₄ (CO) ₁₆ ²⁻ |
| 2 | <i>C</i> _s | 5 | 7 | 3 | 1.40 | 2 | 2 | 1 | 0 | 2 | 5 | (B) 5-Atom Systems B ₅ H ₁₁ |
| 3 | <i>C</i> _{4v} | 5 | 8 | 4 | 1.60 | 0 | 4 | 1 | 0 | 2 | 4 | Square pyramid, ^g Fe ₅ (CO) ₁₅ C, B ₅ H ₅ |
| 4 | <i>C</i> _{3v} | 6 | 9 | 4 | 1.50 | 3 | 0 | 3 | 0 | 2 | 6 | (C) 6-Atom Systems "Opened tetrahedron" |
| 5 | <i>C</i> _{5v} | 6 | 10 | 5 | 1.67 | 0 | 5 | 0 | 1 | 2 | 5 | Pentagonal pyramid, ^g B ₅ H ₁₀ |
| 6 | <i>C</i> _{2v} | 6 | 11 | 6 | 1.83 | 0 | 2 | 4 | 0 | 2 | 4 | Diagonally deficient cube ^{d,g} |
| 7 | <i>C</i> _s | 7 | 11 | 5 | 1.57 | 3 | 0 | 3 | 1 | 2 | 7 | (D) 7-Atom Systems |
| 8 | <i>C</i> _{3v} | 7 | 12 | 6 | 1.71 | 3 | 1 | 0 | 3 | 2 | 6 | "Opened trigonal bipyramid" (<i>w</i> = 3) ^e |
| 9 | <i>C</i> _s | 7 | 13 | 7 | 1.86 | 0 | 3 | 3 | 1 | 2 | 5 | |
| 10 | <i>C</i> _{2v} | 7 | 13 | 6 | 1.86 | 0 | 2 | 5 | 0 | 3 | 4, 4 | 4-Capped trigonal prism ^g |
| 11 | <i>C</i> _s | 7 | 14 | 8 | 2.00 | 0 | 1 | 5 | 1 | 2 | 4 | 7,14,9-Polyhedron ^{d,g} |
| 12 | <i>C</i> _{2v} | 8 | 13 | 6 | 1.62 | 4 | 0 | 2 | 2 | 2 | 8 | (E) 8-Atom Systems "Opened trigonal bipyramid" (<i>w</i> = 3) |
| 13 | <i>C</i> _s | 8 | 14 | 7 | 1.75 | 3 | 0 | 3 | 2 | 2 | 7 | |
| 14 | <i>C</i> ₂ | 8 | 14 | 6 | 1.75 | 0 | 4 | 4 | 0 | 3 | 5, 5 | |
| 15 | <i>C</i> _{2v} | 8 | 15 | 8 | 1.87 | 0 | 4 | 2 | 2 | 2 | 6 | |
| 16 | <i>C</i> _s | 8 | 16 | 9 | 2.00 | 0 | 2 | 4 | 2 | 2 | 5 | |
| 17 | <i>D</i> _{4d} | 8 | 16 | 8 | 2.00 | 0 | 0 | 8 | 0 | 3 | 4, 4 | Square antiprism ^g |
| 18 | <i>C</i> _{2v} | 8 | 17 | 10 | 2.12 | 0 | 0 | 6 | 2 | 2 | 4 | 4,4-Bicapped trigonal prism ^{d,g} |
| 19 | <i>C</i> ₃ | 9 | 15 | 7 | 1.67 | 3 | 3 | 0 | 3 | 2 | 9 | (F) 9-Atom Systems |
| 20 | <i>C</i> _{4v} | 9 | 16 | 8 | 1.78 | 4 | 0 | 1 | 4 | 2 | 8 | "Opened octahedron" |
| 21 | <i>C</i> _s | 9 | 17 | 9 | 1.89 | 1 | 2 | 6 | 0 | 2 | 7 | |
| 22 | <i>C</i> ₂ | 9 | 17 | 8 | 1.89 | 0 | 2 | 7 | 0 | 3 | 5, 5 | |
| 23 | <i>C</i> _{3v} | 9 | 18 | 10 | 2.00 | 0 | 3 | 3 | 3 | 2 | 6 | Icosahedron less three cofacial atoms |
| 24 | <i>C</i> _s | 9 | 19 | 11 | 2.11 | 0 | 2 | 3 | 4 | 2 | 5 | |
| 25 | <i>C</i> _{2v} | 9 | 19 | 10 | 2.11 | 0 | 4 | 1 | 4 | 3 | 4, 4 | 3,4,3-Tricapped trigonal prism ^{d,g} |
| 26 | <i>C</i> _{2v} | 9 | 20 | 12 | 2.22 | 0 | 0 | 5 | 4 | 2 | 4 | 4-Capped square antiprism ^{d,g} |
| 27 | <i>C</i> _s | 10 | 17 | 8 | 1.70 | 2 | 3 | 4 | 1 | 2 | 10 | (G) 10-Atom Systems ⁱ |
| 28 ^h | <i>C</i> _s | 10 | 18 | 9 | 1.80 | 4 | 0 | 2 | 4 | 2 | 9 | |
| 29 | <i>C</i> ₂ | 10 | 18 | 8 | 1.80 | 0 | 4 | 6 | 0 | 3 | 6, 6 | |
| 30 | <i>C</i> _{2v} | 10 | 19 | 10 | 1.90 | 2 | 0 | 6 | 2 | 2 | 8 | Icosahedron less two meta atoms |
| 31 | <i>D</i> _{5d} | 10 | 20 | 10 | 2.00 | 0 | 0 | 10 | 0 | 3 | 5, 5 | Icosahedron less two para atoms ^k |
| 32 | <i>C</i> _{2v} | 10 | 21 | 12 | 2.10 | 0 | 2 | 4 | 4 | 2 | 6 | Icosahedron less two ortho atoms ^k |
| 33 | <i>C</i> _{2v} | 10 | 22 | 12 | 2.20 | 2 | 2 | 6 | 0 | 3 | 4, 4 | 10,22-14-Polyhedron ^{d,g,l} |
| 34 | <i>C</i> _s | 11 | 19 | 9 | 1.73 | 2 | 2 | 7 | 0 | 2 | 11 | (H) Some 11-Atom Systems ^m |
| 35 | <i>C</i> _{5v} | 11 | 20 | 10 | 1.82 | 5 | 0 | 0 | 6 | 2 | 10 | "Opened pentagonal bipyramid" |
| 36 | <i>C</i> ₂ | 11 | 21 | 10 | 1.91 | 0 | 2 | 9 | 0 | 3 | 6, 6 | |
| 37 | <i>C</i> _{2v} | 11 | 24 | 12 | 2.18 | 0 | 0 | 7 | 4 | 4 | 4, 4, 4 | Tricapped cube ^{d,g,l} |
| 38 | <i>C</i> _{5v} | 11 | 25 | 15 | 2.27 | 0 | 0 | 5 | 6 | 2 | 5 | Icosahedron less one atom ⁿ |
| 39 | <i>C</i> _{2v} | 11 | 25 | 14 | 2.27 | 2 | 1 | 8 | 0 | 3 | 4, 4 | Staggered 1442 stack ^{d,g,l} |
| 40 | <i>D</i> _{6d} | 12 | 24 | 12 | 2.00 | 0 | 0 | 12 | 0 | 3 | 6, 6 | (I) Some 12-Atom Systems ^m |
| 41 | <i>D</i> _{4h} | 12 | 28 | 16 | 2.33 | 0 | 0 | 4 | 8 | 3 | 4, 4 | Tetracapped cube ^{d,g,l} |

^a This table considers possible polyhedral networks with 12 or fewer vertices, with no vertices of order six or greater, with at least two triangular faces, and with every triangular face connected to rest of the network by at least a common edge. No vertices are present which are not part of at least one triangular face. Polyhedral networks with two holes of different sizes are excluded. ^b These numbers refer to the structures in Figure 1 which are drawn in a manner similar to the structures in Figure 1 of ref 1. The *v*, *e*, and *t* values are indicated in parentheses in Figure 1. ^c The point group assigned to a network assumes that the dihedral angle between all sets of two joined triangular faces is not necessarily 180°, *i.e.*, the networks, even those with relatively small numbers of edges, are not necessarily planar. ^d For an explanation of the terminology and symbols, see R. B. King, *J. Amer. Chem. Soc.*, **91**, 7211 (1969). ^e See text for an explanation of *h* (connectivity), *z* (edges around hole), and *w* (order of vertex where "opening" takes place). ^f Obvious names for the networks are given here. In a few cases, an example of a known compound with a metal cluster in the network under consideration is given. ^g These polyhedra represent the indicated networks if faces with four or more edges (sides) represent holes. ^h A more symmetrical *C*_{3v} 10,18,9 network is possible (structure 28A in Figure 1), but this has three vertices of order six. ⁱ This network corresponds to the pentagonal antiprism. ^j The 10,20,11-, 10,22,13-, and 10,23,14-polyhedral networks are excluded because they would contain one or more vertices of order six or greater. ^k This polyhedral network is found in decaborane, B₁₀H₁₄. ^l For more detailed information on these polyhedra, see R. B. King, *J. Amer. Chem. Soc.*, **92**, 6460 (1970). ^m Because of the complexities of the 11- and 12-atom systems, only a few of the more symmetrical possible triangulated polyhedral networks for these systems are given. Many possible combinations of *v*, *e*, and *t* values for the 11- and 12-atom systems are excluded because they have one or more vertices of order six or greater. ⁿ This polyhedral network is found in the C₂B₉H₁₁²⁻ anion and related systems.

listed relationships among the parameters describing closed convex three-dimensional polyhedra with only

triangular and quadrilateral faces. The following are the analogous relationships among the parameters de-

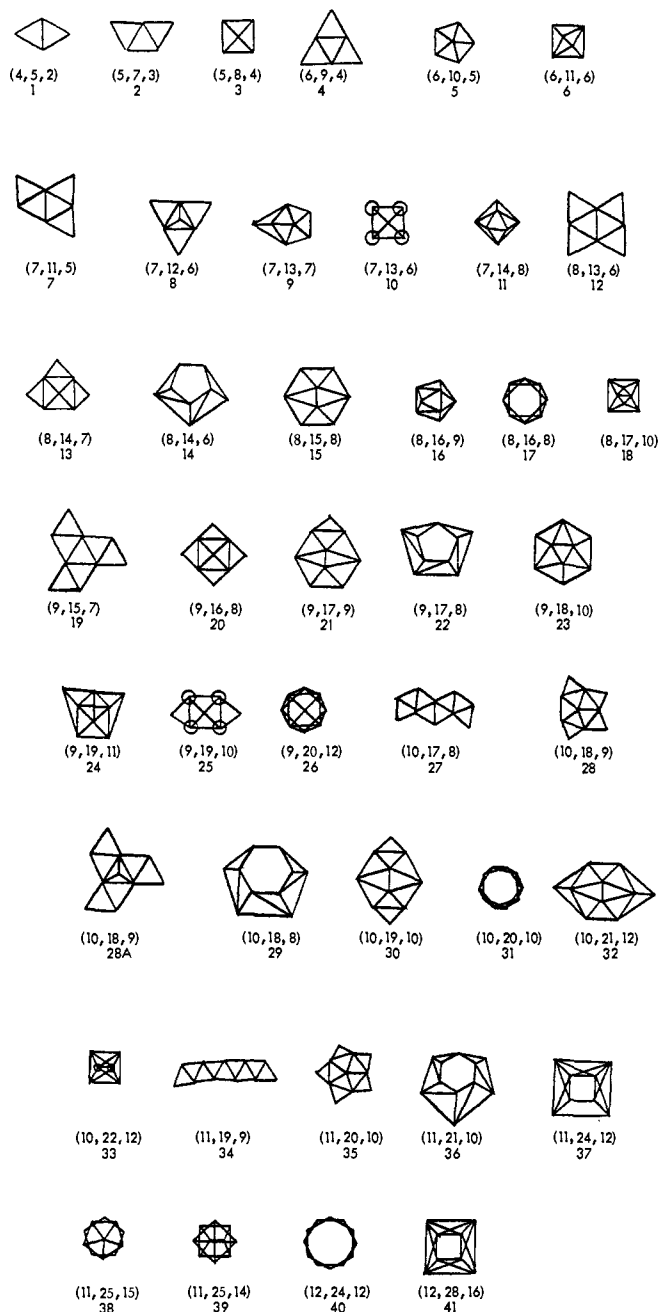


Figure 1. Two dimensional representations of some triangulated polyhedral networks.

scribing open three-dimensional polyhedra with only triangular faces:¹⁶ (1) generalized Euler's relationship,¹⁵ $v + t - e = 3 - h$ (for the case of closed polyhedra of unit connectivity, this reduces to the familiar form of Euler's relationship $e + 2 = v + f$); (2) relationship between the edges and faces, $2e \geq 3t$ (this relationship arises from the fact that each edge is shared by no more than two faces and that all faces have three edges or half-edges; the equality only holds for closed triangulated polyhedra); (3) relationship between the edges and vertices, $\sum_{i,j} t_{ij} = 2e$ (this relationship arises from the fact that each edge connects exactly two vertices); (4) relationship between the vertices and faces,

(16) Since some of these relationships apply only to polyhedra with only triangular faces (triangulated polyhedra), the parameter t (as defined in ref 9) rather than the parameter f is used to indicate the number of faces.

$t > v - 2$ (see the Appendix for a derivation of this relationship); (5) totality of vertices, $\sum_{i,j} t_{ij} = v$; (6) total number of edges bordering holes, $Z = 2e - 3t$ (see the Appendix for a derivation of this relationship); (7) distribution of the total number of edges bordering holes among the available holes, $Z = \sum_{i,j} z_{ij}$; (8) size of holes, $z_n \geq 4$ for all n (no hole can have only three edges for polyhedral fragments representing either metal clusters or boron hydrides, since all triangular faces remain closed because of strong interaction among the three metal-metal bonds forming a triangle in a metal cluster¹¹ or strong three-center bonding among a triad of boron atoms at the vertices of a triangle); and (9) maximum connectivity for a given number of vertices and faces, $2h \leq 2v - t - 2$ (see the Appendix for a derivation of this relationship).

Using these relationships, possible open triangulated polyhedral fragments may be generated by selecting a number of vertices corresponding to the number of atoms in the cluster of interest and then determining numbers of edges and faces which satisfy the generalized Euler's relationship and the inequalities $2e \geq 3t$ and $t \geq v - 2$ discussed above, considering systems only with connectivities satisfying the relationship $2h \leq 2v - t - 2$. The other properties of the polyhedral fragments generated can be determined from the other relationships given above. Determination of the symmetry point group of the resulting polyhedral fragments is aided by the requirement that the order of the principal rotation axis must be evenly divisible into the numbers of edges bordering each hole (*i.e.*, each z_n). In determining the symmetry point groups of the polyhedral fragments generated, the fusion of all pairs of connected triangular edges is assumed to be nonplanar.

Table III summarizes the properties of the open triangulated polyhedral fragments for clusters of 4-10 metal atoms and a few such fragments for 11- and 12-atom clusters excluding from consideration polyhedral fragments of the following types: (1) open triangulated polyhedral fragments with two or more holes of different sizes, since such fragments possess little or no symmetry and bear little resemblance to known metal clusters and (2) open triangulated polyhedral fragments with one or more vertices of order six or greater, since utilizing six hybrid orbitals of a given metal atom to bond to six other metal atoms in the same polyhedral fragment is expected to lead either to excessive strain or to higher coordination numbers than have been otherwise demonstrated for the metal atoms forming clusters. The second restriction eliminates many of the otherwise possible polyhedral fragments for 11- and 12-atom clusters. Since many of the triangulated polyhedral fragments in Table III have no obvious names, they are depicted schematically in Figure 1. Some of the triangulated polyhedral fragments in Table III correspond to previously encountered closed coordination polyhedra^{1,9} with one to three faces with four or more edges and the remainder of the faces triangular. In these cases, the faces with four or more edges (quadrilaterals, pentagons, hexagons, etc.) in the closed coordination polyhedra correspond to the holes in the open triangulated polyhedral networks in Table III. However, only closed polyhedra with a sufficiently large percentage of triangular faces can correspond to the open triangulated polyhedral networks of Table III, for the

number of triangular faces in the network must be sufficient for each triangle of the network to share a common edge with an adjacent triangle. This relates to the maximum connectivity restriction $2h \leq 2v - t - 2$ and the direct relationship between the connectivity and the number of holes of the polyhedral fragment $h = H + 1$; the number of holes, H , in the polyhedral fragment is identical with the number of faces with four or more edges in the corresponding coordination polyhedron. Table III also lists the e/v values for the open triangulated polyhedral networks which for metal clusters directly correspond to the numbers of metal-metal bonds per metal atom. The stability of the open triangulated polyhedral fragment should increase with increasing values of the ratio e/v . In all cases the ratio e/v is less for any open triangulated polyhedral networks than for the closed triangulated polyhedron (Table II) with the same number of vertices. This suggests that open triangulated polyhedral networks (Table III) will only be found for metal clusters, where electronic or steric factors inhibit closure to form closed triangulated polyhedra. Such closure inhibition can arise from a bridging group "propping open" the hole of an open fragment like the carbide carbon in $\text{Fe}_5(\text{CO})_{15}\text{C}^{17}$ or the bridging acetylene in $\text{Co}_4(\text{CO})_{10}\text{C}_2\text{R}_2$ derivatives¹⁸ or by limitation in the number of electrons available for metal-metal bonding, as in $\text{Re}_4(\text{CO})_{16}^{2-}$.¹⁹

Some of the open triangular polyhedral networks in Table III have other properties of interest. Certain such open triangulated polyhedral networks (the 9,18, 10-, 10,19,10-, 10,20,10-, 10,21,12-, and 11,25,15-polyhedral fragments) may be generated from the regular icosahedron by removal of one, two, or three atoms, similar to the generation of the square pyramid (the open 5,8,4-polyhedral network (Table III) or the closed 5,8,5-polyhedron⁹) by removal of one atom from the regular octahedron. Other open triangulated polyhedral networks arise by "opening" a closed triangulated polyhedron. This opening process refers to pulling apart symmetrically all faces joined at a vertex of a closed polyhedron as if to retrieve an object imprisoned in the center of the polyhedron; open polyhedral fragments of the highest symmetry are obtained if the vertex where the opening process takes place is located on the highest order rotation axis, for this rotation axis then is not lost because of the symmetry of the pulling apart operation. If the subscripts c and o refer to the original closed triangulated polyhedron and the new open triangulated polyhedral fragment obtained by the opening process, respectively, and if w refers to the order of the vertex where the opening takes place, the following relationships are satisfied: $v_o = v_c + w - 1$; $e_o = e_c + w$; and $f_o = f_c$.

Most syntheses of metal cluster compounds utilize the oligomerization of a coordinatively unsaturated intermediate containing fewer metal atoms than the desired cluster.⁵ A process of this type would be expected to yield cluster compounds in which all metal atoms are in similar environments, including the same number of metal-metal bonds to other metal atoms in the cluster. The polyhedra for metal clusters formed in this manner would be expected to have all vertices of

the same order. Such polyhedra may be called isoordinal polyhedra. In the case of closed *triangulated* polyhedra, the parameters describing isoordinal polyhedra may be obtained by using the relationship $2n = e[2 - (n/3)]$, where n is the order of the vertices of the closed triangulated isoordinal polyhedron and can be 3, 4, or 5. In this manner the isoordinal triangulated polyhedra can be shown to be the tetrahedron, the octahedron, and the icosahedron, which are also the three of the five classical regular polyhedra which have triangular faces.²⁰

Systematic generation of isoordinal open polyhedral fragments of nonunit connectivity is considerably more complex and of minor importance for the chemistry discussed in this paper. However, inspection of Table III reveals the first three members of a series of isoordinal open polyhedral fragments with connectivity three derived from the regular antiprisms (staggered nm stacks¹ with $n=4$). All vertices of these regular antiprisms have order 4, and their parameters v , e , and t are related by the equations $v = t = 2n$ and $e = 4n$. These antiprismatic clusters are related to the torus as the normal closed triangulated polyhedra are related to the sphere. No compounds based on these toroidal antiprismatic clusters are known; such compounds may be preparable by taking a spherical or nearly spherical atom or molecule with the bonding sites distributed as a ring around the sphere and surrounding it by a cluster of metal atoms.

Metal Cluster Compounds

With the exception of the seven-atom $\text{Rh}_7(\text{CO})_{18}^{3-}$ cluster, all known true clusters of transition metals contain six or fewer metal atoms and correspond to polyhedra or polyhedral fragments with no vertices of order higher than four. Thus, no transition metal clusters are derived from the icosahedron, the isoordinal closed polyhedron with vertices of order five. The triangle, tetrahedron, and octahedron predominate in metal cluster chemistry, since they are the isoordinal closed polyhedra with vertices of orders two, three, and four, respectively.

The bonds from a given cluster metal atom to other metal atoms of the same cluster must all be entirely located on one side of a supporting plane (stutzeben)²¹ of the polyhedron passing through the metal atom in question. Thus only half of the possible spatial directions are available for these bonds. In the absence of excessive angular strain,²² a metal bonded to m other metal atoms in a closed polyhedral cluster on one side of a supporting plane of the polyhedron passing through the metal atom in question must form $m - 1$ bonds to atoms outside the polyhedral cluster on the other side of this supporting plane. This implies that a metal atom located at a vertex of order m in a metal cluster in the absence of excessive angular strain must have a minimum coordination number of $m + (m - 1) = 2m - 1$. Hence, a metal atom located in a vertex of order five of

(20) Reference 15, pp 89-93.

(21) A. D. Alexandrow, "Konvexe Polyeder," Akademie-Verlag, Berlin, 1958, p 14.

(22) Excessive angular strain as used here refers to significant deviation from the normal angles of a coordination polyhedron because of other constraints, generally steric, present in the molecule under consideration. Cyclopropane and cyclobutane are excellent examples of derivatives of tetrahedral carbon atoms which exhibit significant angular strain.

(17) E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Amer. Chem. Soc.*, **84**, 4633 (1962).

(18) L. F. Dahl and D. L. Smith, *ibid.*, **84**, 2450 (1962).

(19) M. R. Churchill and R. Bau, *Inorg. Chem.*, **7**, 2606 (1968).

a polyhedral metal cluster would have a minimum coordination number of nine. Coordination numbers this high are rare among transition metals that normally form metal clusters, particularly since the sp^3d^5 hybrid (in the absence of suitable f orbitals) leaves no filled d orbitals to participate in retrodative bonding, which contributes to the stability of metal cluster compounds, particularly those containing carbonyl groups. This reluctance of metal atoms to locate at a vertex of order five or more in a cluster polyhedron limits the size of closed polyhedral metal clusters to six metal atoms, where the octahedron is a very favorable cluster polyhedron.

On the basis of the general considerations discussed in this paper, the polyhedra and polyhedral fragments for metal clusters of different sizes will now be treated separately.

(1) Clusters of Three Metal Atoms. The only possible cluster with three metal atoms is the triangle. Many trinuclear derivatives containing metal triangles are known, such as $Ru_3(CO)_{12}$, $Re_3Cl_{12}^{3-}$, $[C_5H_5RhCO]_3$, etc.³⁻⁵ The triangle is the isoordinal polyhedron with vertices of order two. For this reason, many mononuclear transition metal units with a 16-electron configuration,²³ especially those with carbonyl groups such as $M(CO)_4$ ($M = Fe, Ru, \text{ and } Os$) and C_5H_5MCO ($M = Co \text{ and } Rh$), form trimers containing metal triangles and possessing the favored 18-electron rare-gas configuration.

(2) Clusters of Four Metal Atoms. The closed triangulated polyhedral cluster with four metal atoms is the tetrahedron, which is also the isoordinal triangulated polyhedron with vertices of order three. A variety of tetranuclear metal derivatives containing metal tetrahedra are known, such as $Ir_4(CO)_{12}$, (azulene)- $Ru_4(CO)_9$, etc.³⁻⁵ Mononuclear transition metal units with a 15-electron configuration,²³ especially those with carbonyl groups such as $M(CO)_5$ ($M = Co, Rh, \text{ and } Ir$) and C_5H_5MCO ($M = Fe \text{ and } Ru$), often form tetramers containing metal tetrahedra and possessing the favored 18-electron rare-gas configuration.

In the case of a four-metal-atom cluster, the open 4,5,2-polyhedral fragment (structure 1 in Figure 1) is also possible. This polyhedral fragment is found in tetranuclear cobalt-acetylene complexes¹⁸ of the type $Co_4(CO)_{10}C_2R_2$, where the alkyne blocks closure to a tetrahedron, and in the tetranuclear rhenium carbonyl anion²¹ $Re_4(CO)_{16}^{2-}$, where there are only sufficient electrons available for 5 rather than 6 rhenium-rhenium bonds after forming the 16 rhenium-carbon bonds and giving each rhenium atom the favored 18-electron rare-gas configuration.²³

(3) Clusters of Five Metal Atoms. The closed triangulated polyhedron with five vertices is the trigonal pyramid, which is *not* isoordinal. The only examples of this polyhedron in a metal cluster are the recently reported²⁴ $[M_2Ni_3(CO)_{16}]^{2-}$ ($M = Mo \text{ or } W$) anions. Two open polyhedral fragments with five vertices are possible (Table III). The open polyhedral fragment with five vertices and the maximum number of edges is the C_{4v} 5,8,4 fragment derived from the square pyramid. This fragment is found in the iron carbonyl carbide

(23) R. B. King, *Advan. Chem. Ser.*, No. 62, 203 (1967).

(24) J. K. Ruff, R. P. White, Jr., and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 2159 (1971).

$Fe_6(CO)_{15}C$, where the extra carbon atom is inserted into the square hole to keep it open.¹⁷

(4) Clusters of Six Metal Atoms. The closed triangulated polyhedral cluster with six metal atoms is the octahedron, which is also the isoordinal triangulated polyhedron with vertices of order four. Numerous octahedral metal clusters are known, including $[(M_6X_{12})L_6]^{n+}$ ($M = Nb \text{ or } Ta, X = \text{halogen}, L = \text{neutral Lewis base ligand}, n = 2 \text{ or, less favorably, } 3 \text{ and } 4$),²⁵ $[(M_6X_6)L_6]^{4+}$ ($M = Mo \text{ or } W$),^{3,26} $M_6(CO)_{16}$ ($M = Co,^{27} Rh,^{28} \text{ and } Ir^{29}$) and anions derived from the cobalt and rhodium carbonyl octahedra, and $Ru_6C(CO)_{17}$ and its arene π complexes.³⁰ The 12-atom system $[Rh_{12}(CO)_{30}]^{2-}$ consists of two metal octahedra joined by a metal-metal bond supported by two bridging carbonyl groups;³¹ its structure thus has a similar relationship to simple metal octahedra as biphenyl has to benzene.

No six-metal-atom clusters based on open polyhedral fragments are known.

(5) Clusters of Seven Metal Atoms. There are two isogonal closed triangulated polyhedra with seven vertices of different point groups, the D_{5h} pentagonal bipyramid and the C_{3v} capped octahedron (Table II). A cluster of seven metal atoms could conceivably be based on either of these polyhedra, but both polyhedra have vertices of order five and hence are unfavorable for transition metal clusters. The only authentic example³² of a seven-metal-atom cluster presently known is the rhodium carbonyl anion $Rh_7(CO)_{16}^{3-}$, which is based on the capped octahedron.

(6) Clusters of Eight Metal Atoms. The one known apparent eight-atom cluster is the copper(I) 1,1-dicyanoethylene-2,2-dithiolate derivative $\{Cu_8[S_2CC(CN)_2]_6\}^{4-}$, in which X-ray studies³³ show the copper atoms to be arranged at the corners of a cube. However, this system also has sulfur atom bridges along each of the 12 edges of the metal cube. The relatively long copper-copper distance in this copper cube³³ suggests relatively weak copper-copper bonding with copper-sulfur bonds rather than copper-copper bonds being largely responsible for holding the cube together. This is consistent with the availability of only 16 electrons for copper-copper bonding in the 8-copper system, corresponding to only 8 copper-copper bonds. The geometry of the octametallate complex $\{Cu_8[S_2CC(CN)_2]_6\}^{4-}$ thus arises more from the electronic and steric requirements of the bridging sulfur ligands than from the metal-metal bonding; the treatment of this paper thus does not pertain to this type of system.

Polyhedral Boron Hydrides and Carboranes

Many theoretical aspects of the chemistry of boron hydrides have already been treated in some detail in the

(25) R. D. Burbank, *Inorg. Chem.*, **5**, 1491 (1966), and references cited therein.

(26) F. A. Cotton, R. M. Wing, and R. A. Zimmermann, *ibid.*, **6**, 11 (1967), and references cited therein.

(27) P. Chini, *ibid.*, **8**, 1206 (1969).

(28) E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, **85**, 1202 (1963).

(29) L. Malatesta, G. Caglio, and M. Angoletta, *Chem. Commun.*, 532 (1970).

(30) B. F. G. Johnson, R. D. Johnston, and J. Lewis, *ibid.*, 1057 (1967).

(31) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 299 (1969); V. G. Albano and P. L. Bellon, *J. Organometal. Chem.*, **19**, 405 (1969).

(32) P. Chini and S. Martinengo, *Chem. Commun.*, 1092 (1969); V. G. Albano, P. L. Bellon, and G. F. Ciani, *ibid.*, 1024 (1969).

(33) L. E. McCandlish, E. C. Bissell, D. Coucouvannis, J. P. Fackler, and K. Knox, *J. Amer. Chem. Soc.*, **90**, 7357 (1968).

literature,^{6,7} including a topological theory³⁴ leading to relationships among the numbers of various structural units of boron hydrides such as three-center boron–boron–boron bonds, BH₂ groups, bridging hydrogen atoms, etc. The theory of polyhedral metal clusters developed in this paper supplements the available theoretical work on polynuclear boron hydrides by providing a facile method for evaluating the stabilities of different possible polyhedra for B_nH_n²⁻, C₂B_{n-2}H_n, and similar systems.

A boron atom has only one s orbital and three p orbitals available for bonding; these can hybridize to form four tetrahedral sp³ orbitals. A BH group located at a vertex of order three (structure I in Figure 2) can utilize the available three of the four boron sp³ hybrid orbitals for normal two-center bonds with the three boron atoms bonded to the vertex in question. However, for BH groups located at vertices of order four, five, or six (structures II, III, and IV in Figure 2) some three-center bonding is necessary to join the BH group in question to all of the neighboring boron atoms. Furthermore, in these cases of BH groups located at vertices of order four, five, or six, two or more canonical structures can be drawn (Figure 2) based on different ways of distributing the two-center and three-center bonds between the BH group in question and the neighboring boron atoms. This suggests the possibility of resonance stabilization through bond delocalization in these cases. Furthermore, all of the canonical structures listed in Figure 2 for a BH group at a vertex of given order are identical structures in that any one such canonical structure can be converted to any other canonical structure by an appropriate amount of rotation about an axis passing through the vertex under consideration. This means that each of the canonical structures listed in Figure 2 for a BH group at a vertex of given order is of equal energy. Hence, the degree of resonance stabilization for a BH group at a vertex of given order increases monotonically as the number of equivalent canonical structures is increased.³⁵ On this basis, a BH group located at a vertex of order five has a relatively large amount of such resonance stabilization in its bonds to other boron atoms; a BH group located at a vertex of order four has slightly less such resonance stabilization; a BH group located at a vertex of order six has much less but still noticeable amounts of such resonance stabilization; and a BH group located at a vertex of order three has no such resonance stabilization. Furthermore, even by using all three-center boron–boron–boron bonds, a BH group cannot bond to seven or more boron atoms, thereby preventing a BH group from being located at a vertex of order seven or higher. In addition, polyhedra with one or more faces with four or more sides (nontriangulated polyhedra⁹) are unsatisfactory models for cage boron hydride structures, since boron–boron–boron three-center bonding involving three of the boron atoms at vertices of a face with four or more sides is impossible or at least very unfavorable because the interatomic distance between at least one pair of three such boron atoms would be too large (see Table 1).

(34) W. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

(35) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Interscience, New York, N. Y., pp 81–84.

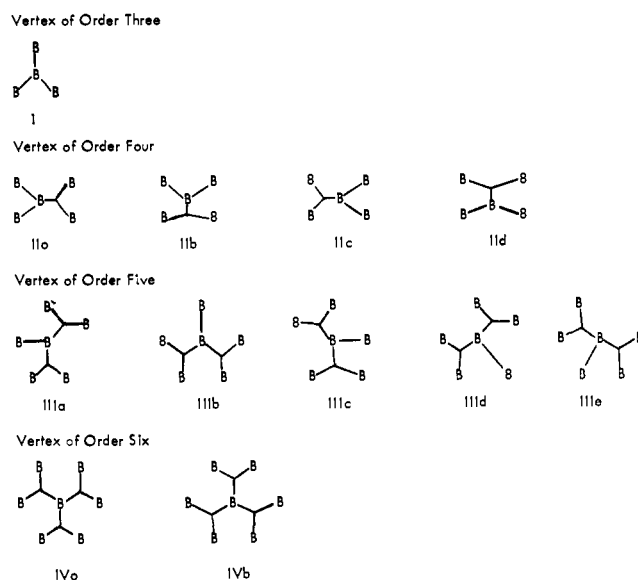


Figure 2. Some possible canonical structures for BH groups at vertices of various orders in closed polyhedra of cage boranes (B = BH in these structures).

The considerations discussed above relate to the magnitudes of resonance stabilization energies and hence pertain to the thermodynamic stability of boron hydride cages. They thus relate to decisions among different possible polyhedra for cages of a given number of boron atoms. However, stabilities of boron hydrides are often determined by measurement of their degradation in water or similar hydroxylic solvents under various conditions. In considering such hydrolytic stabilities of boron hydrides, the thermodynamic stability factors cited above must be supplemented by kinetic stability factors. In particular, the availability of sites in the boron cage to attack by water or hydroxylic solvents must be considered. Simple steric considerations suggest that the lower the order of the vertex at which a boron atom is located, the more susceptible that boron atom is to attack by water or other hydroxylic solvents since it "sticks out" more because of the angles involved.

These factors permit the application of the theory of polyhedra discussed in this paper to two important questions in the chemistry of polynuclear boron hydrides. (1) Which of the possible polyhedra will be favored for a cage of a given number of boron atoms? Simple considerations discussed above permit consideration of only triangulated polyhedra for boron hydride cage structures. Thus, there is only real uncertainty when two or more isogonal triangulated polyhedra with different symmetry properties exist for a given number of vertices (clearly the case for polyhedra of 7, 8, 9, 10, and 11 boron atoms). (2) What will be the relative stabilities of cages containing different numbers of boron atoms? The first question concerning possible polyhedra for cages with various numbers of boron atoms will first be considered.

(1) Cages of 5 Boron Atoms. The only possible closed triangulated polyhedron for the five-boron system is the D_{3h} trigonal bipyramid. This polyhedron is found in the five-atom carborane C₂B₃H₅ and its derivatives.³⁶ The anion B₅H₅²⁻ is unknown.

(36) I. Shapiro, C. D. Good, and R. E. Williams, *J. Amer. Chem. Soc.*, **84**, 3837 (1962).

(2) **Cages of 6 Boron Atoms.** The only possible closed triangulated polyhedron for the six-boron system is the octahedron. This polyhedron is found in the $B_6H_6^{2-}$ anion³⁷ and in the six-atom carborane $C_2B_4H_6$ and its derivatives.³⁸

(3) **Cages of 7 Boron Atoms.** The two possible closed triangulated polyhedra for seven-boron systems are the D_{3h} pentagonal bipyramid and the C_{3v} capped octahedron (Table II). The capped octahedron has one vertex of order three, whereas the pentagonal bipyramid has no vertices of order three. Since BH groups at vertices of order three cannot participate in bond delocalization of the type discussed above, the pentagonal bipyramid is a more favorable polyhedron for the seven-boron system than the capped octahedron. This is consistent with the observation of the pentagonal bipyramid in both the anion³⁹ $B_7H_7^{2-}$ and in derivatives of the seven-atom carborane $C_2B_5H_7$.⁴⁰

(4) **Cages of 8 Boron Atoms.** The two possible closed triangulated polyhedra for eight-boron systems are the D_{3d} bicapped octahedron and the D_{2d} dodecahedron (Table II). The bicapped octahedron has two vertices of order three, whereas the D_{2d} dodecahedron has no vertices of order three. For reasons similar to the seven-atom case, the D_{2d} dodecahedron is a more favorable polyhedron for the eight-boron system than the bicapped octahedron. This is consistent with the observation of the D_{2d} dodecahedron in both the anion⁴¹ $B_8H_8^{2-}$ and in derivatives of the eight-atom cage carborane $C_2B_6H_8$.⁴²

(5) **Cages of 9 Boron Atoms.** The two possible closed triangulated polyhedra for nine-boron systems are the D_{3h} 4,4,4-tricapped trigonal prism and the C_{2v} staggered 252 stack¹ (Table II). The C_{2v} staggered 252 stack has two vertices of order six, whereas the D_{3h} 4,4,4-tricapped trigonal prism has no vertices of order six. Since BH groups at vertices of order six participate in bond delocalization to a much lesser extent than BH groups at vertices of orders four and five, as discussed above, the D_{3h} 4,4,4-tricapped trigonal prism is a more favorable polyhedron for the nine-boron system than the C_{2v} staggered 252 stack. This is consistent with the observation of the D_{3h} 4,4,4-tricapped trigonal prism in both the anion⁴³ $B_9H_9^{2-}$ and in derivatives of the nine-atom cage carborane $C_2B_7H_9$.⁴⁴

(6) **Cages of 10 Boron Atoms.** The two possible closed triangulated polyhedra for ten-boron systems are the D_{4d} 4,4-bicapped square antiprism and the C_{3v} 3,4,4,4-tetracapped trigonal prism (Table II). The 3,4,4,4-tetracapped trigonal prism has one vertex of order three, whereas the 4,4-bicapped square antiprism has no vertices of order three. For reasons similar to the seven-boron case, the 4,4-bicapped square antiprism is a more favorable polyhedron for the ten-boron system than the 3,4,4,4-tetracapped trigonal prism. This is consistent with the observation of the 4,4-bi-

capped square antiprism in both the anion⁴⁵ $B_{10}H_{10}^{2-}$ and in derivatives of the ten-atom cage carborane $C_2B_8H_{10}$.⁴⁶

(7) **Cages of 11 Boron Atoms.** All closed triangulated polyhedra with 11 vertices have at least one vertex of order six (Table II). The highest symmetry triangulated 11-vertex polyhedron, the D_{3h} pentacapped trigonal prism, has six vertices of order six and two vertices of order three; as discussed above, vertices of order three and six are both unfavorable relative to vertices of orders four and five in cage borane polyhedra. This accounts for the observation that both the $B_{11}H_{11}^{2-}$ anion⁴⁷ and derivatives of the 11-atom cage carborane⁴⁸ $C_2B_9H_{11}$ utilize a less symmetrical C_{2v} closed triangulated 11-atom polyhedron which has no vertices of order three and only one vertex of order six. The 11-boron system is the only closed boron cage based on a polyhedron with a vertex of order six. This may account for the strong Lewis acid characteristics of the 11-atom cage carborane $C_2B_9H_{11}$, which readily reacts with Lewis bases such as pyridine and triphenylphosphines to give adducts of the type $C_2B_9H_{11}L$ (L = Lewis base ligand) based on the C_{3v} 11,25,15 11-atom open icosahedral fragment⁴⁶ which contains no vertices of order six.

(8) **Cages of 12 Boron Atoms.** The only possible closed triangulated polyhedron without vertices of order six for the 12-atom system is the highly symmetrical icosahedron with all vertices of order five (Table II). The icosahedron is found in both the anion⁴⁹ $B_{12}H_{12}^{2-}$ and in the three isomeric 12-atom cage $C_2B_{10}H_{12}$ carboranes and their derivatives.^{6,7}

(9) **Cages of More than 12 Boron Atoms.** All possible closed triangulated polyhedra with more than 12 vertices have at least one vertex of order six or higher and are thus very unfavorable polyhedra for cage boron hydrides. No boron derivatives with cages of more than 12 boron atoms are known. Boron derivatives containing more than 12 boron atoms (*e.g.*, $B_{18}H_{22}$ ⁵⁰ and $B_{20}H_{18}$ ⁵¹) all have structures based on two or more linked polyhedra or polyhedral fragments containing 12 or fewer boron atoms.

The properties of closed triangulated polyhedra discussed in this paper also account for the relative stabilities of boron hydrides with different size cages. Thus the polyhedral boron hydride derivatives generated by heating borohydrides and borane adducts in the presence of bases⁵² include species such as $B_{12}H_{12}^{2-}$, which is based on the icosahedron with all vertices of the favorable order five as discussed above.⁴⁹ The hydrolytic stabilities of the different $B_nH_n^{2-}$ anions are reported^{39,47} to decrease in the following sequence: $B_{12}H_{12}^{2-}$ (greatest) $>$ $B_{10}H_{10}^{2-}$ \gg $B_{11}H_{11}^{2-}$ $>$ $B_9H_9^{2-}$ \sim $B_8H_8^{2-}$ \sim $B_6H_6^{2-}$ \gg $B_7H_7^{2-}$ (least). The monotonic decrease

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(49) J. A. Wunderlich and W. N. Lipscomb, *ibid.*, **82**, 4427 (1960).

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(51) N. E. Miller and E. L. Muetterties, *J. Amer. Chem. Soc.*, **85**, 3506 (1963); *Inorg. Chem.*, **3**, 1690 (1964); R. D. Dobrott, L. F. Friedman, and W. N. Lipscomb, *J. Chem. Phys.*, **40**, 866 (1964).

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(41) L. J. Guggenberger, *Inorg. Chem.*, **8**, 2771 (1969).

(42) H. Hart and W. N. Lipscomb, *ibid.*, **7**, 1070 (1968).

(43) L. J. Guggenberger, *ibid.*, **7**, 2260 (1968).

(44) T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *ibid.*, **7**, 1076 (1968).

in hydrolytic stability in going from $B_{10}H_{10}^{2-}$ to $B_7H_7^{2-}$ is a consequence of the gradual substitution of vertices of order four for vertices of order five in cage polyhedra; a boron atom at a vertex of order four is less protected from attack by water or similar species than a boron atom at a vertex of order five. The lower hydrolytic stability of $B_{11}H_{11}^{2-}$ relative to both $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ may be a consequence of the presence of the unique vertex of order six in the 11-atom cage which lowers its stability by partial inhibition of resonance. The abnormally high hydrolytic stability of octahedral $B_6H_6^{2-}$ with all vertices of order four relative to the low hydrolytic stability of $B_7H_7^{2-}$ with two vertices of the more favorable order five may be a consequence of the very high symmetry of the octahedral $B_6H_6^{2-}$ which results in no charge separation and hence no preferential site for attack by water or similar reagents. The five-boron cage anion $B_5H_5^{2-}$ based on the trigonal bipyramid is unknown. This theory predicts that $B_5H_5^{2-}$ would be much less stable hydrolytically than even the very unstable $B_7H_7^{2-}$ because of the presence of two vertices of order three at the apices of the trigonal bipyramid. The boron atoms at these vertices of order three cannot participate in resonance stabilization like the boron atoms at vertices of higher order and furthermore are relatively unprotected from attack by reagents such as water. Indeed, a $B_5H_5^{2-}$ salt such as $Na_2B_5H_5$ might resemble on alkylmagnesium or alkylaluminum compound in its sensitivity to hydrolysis.

Many of the open triangulated polyhedral networks listed in Table III are found in various open polynuclear boron hydride derivatives. Perhaps the most striking observation in this area of chemistry is the tendency for decaborane, $B_{10}H_{14}$, to be the major pyrolysis product of lower boranes.⁵³ The topological theory of boron hydrides³⁴ demonstrates that stable neutral boron hydride fragments based on a single polyhedral fragment must have more hydrogen atoms than boron atoms. Thus stable neutral boron hydrides must have BH_2 groups and/or bridging hydrogen atoms. These structural units cannot be accommodated in a closed polyhedral structure, since insufficient boron orbitals remain after bonding to two hydrogen atoms to bond to other borons in a closed polyhedron. Thus, only open polyhedra are possible for neutral boron hydrides. The five-sided hole in the 11,25,15 icosahedral fragment can only accommodate enough "extra" hydrogen atoms to give the $B_{11}H_{14}^-$ monoanion.⁵⁴ Only in the case of the ten-atom icosahedral fragments are the holes large enough to accommodate enough "extra" hydrogen atoms to result in a neutral boron hydride derivative. Of the three icosahedral fragments arising from the removal of ortho (1,2), meta (1,7), and para (1,12) pairs of boron atoms from a boron icosahedron, the C_{2v} 10,21,12 fragment (Table III) upon which the structure of decaborane, $B_{10}H_{14}$, is based has the largest number of both edges and faces. The number of possible sites for both two-center and three-center boron-boron intracage bonding is thus maximized in the C_{2v} 10,21,12 fragment relative to the other two ten-atom icosahedral fragments. Decaborane is thus the closest a neutral boron hydride can approach to the favored icosahedron;

(53) A. E. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, pp 80-85.

(54) V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 1, 734 (1962).

this can account for the particular ease of formation and stability of decaborane relative to other neutral boron hydrides.

Appendix

Some of the relationships used in this paper are neither well known nor obvious and hence are derived in this Appendix.

(1) **Relationship between the Vertices and Faces, $t \geq v - 2$.** The minimum number of triangular faces for a given number of vertices in an open triangulated polyhedral fragment is obtained if each triangle shares exactly one edge with another triangle of the fragment. An end triangle of the open triangulated polyhedral fragment with a minimum number of faces contributes three vertices, three edges, and one triangle to the fragment. Fusion of another triangle with this end triangle such that both triangles have exactly one edge in common contributes one more vertex, two more edges, and one more triangle. This same type of fusion can be continued to give a polyhedral fragment with the minimum number of faces for any given number of vertices. In such a fragment with v vertices, the first end triangle contributes three vertices and the next $t - 1$ triangles contribute $t - 1$ vertices leading to the relationship $v = 3 + (t - 1)$ or $t = v - 2$ for a triangulated polyhedral fragment with the minimum of triangular faces for a given number of vertices. Thus, for all triangulated polyhedral fragments $t \geq v - 2$.

(2) **Total Number of Edges Bordering Holes, $Z = 2e - 3t$.** The edges in any triangulated polyhedral fragment are of either of two types: (1) the interior edges joining exactly two triangular faces, the number of which is e_i and (2) the exterior edges joining a triangular face and a hole, the number of which is e_e . The following equations relate the number of triangles and the total number of edges bordering holes to interior and exterior edges as defined above.

$$3t = 2e_i + e_e \quad (1)$$

$$Z = e_e \quad (2)$$

But by definition

$$e = e_e + e_i \quad (3)$$

Adding eq 1 and 2 followed by removal of e_e and e_i by use of eq 3 and rearrangement gives the desired relationship $Z = 2e - 3t$.

(3) **Maximum Connectivity for a Given Number of Vertices and Faces, $2h \leq 2v - t - 2$.** Any hole must have at least four edges (see text). Therefore

$$4H \leq Z \quad (4)$$

Combining this inequality with the equality $Z = 2e - 3t$ derived above in section 2 of the Appendix and with the equality $H = h - 1$ discussed in the text gives the inequality

$$4h - 4 \leq 2e - 3t \quad (5)$$

Rearrangement of the generalized Euler's relationship gives e as the following function of v , t , and h

$$e = v + t + h - 3 \quad (6)$$

Removal of e from eq 5 by using eq 6 followed by rearrangement, collecting terms, and dividing by $+2$ gives the desired relationship $2h \leq 2v - t - 2$.