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Chemical Applications of Group Theory and Topology. 7. A Graph-Theoretical Interpretation of the Bonding Topology in Polyhedral Boranes, Carboranes, and Metal Clusters[1c]

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Abstract: The bonding topology in three-dimensional closed deltahedral systems such as the cage boranes, carboranes, and some metal clusters can be analyzed completely analogously to that in delocalized two-dimensional polygonal systems such as benzene by algebraic graph-theoretical methods. Such methods make use of the complete graphs K_n rather than the cyclic graphs C_n to represent the interactions between the unique internal orbitals of the vertex atoms. This analysis provides a theoretical basis for the stability of closed deltahedral systems with n vertices and $2n + 2$ skeletal electrons. The anomaly of tetrahedral systems in requiring 12 rather than 10 skeletal electrons appears to be a consequence of edge-localized bonding in the tetrahedron arising from the degree three of all of its vertices. This graph-theoretical analysis of bonding topology can also be applied to the electron-rich nido systems with one hole, n vertices, and $2n + 4$ skeletal electrons as well as to less delocalized systems with even more skeletal electrons and holes. Electron-poor polyhedral cluster systems with n vertices and less than $2n + 2$ skeletal electrons form deltahedra with one or more capped faces and normally require transition metals, rather than boron or carbon, at the vertices of the capped faces. Puncture or excision of closed deltahedra to form electron-rich open polyhedra with one or more holes may be considered as opposite or dual to the capping of closed deltahedra to form electron-poor larger deltahedra with tetrahedral chambers.

I. Introduction

One of the most interesting and significant developments in inorganic chemistry during the past two decades has been the discovery of boron cage compounds exhibiting unusually high stability and low chemical reactivity such as the dianions[2,3] $B_nH_n^{2-}$ $(6 \le n \le 12)$, and the carboranes[4] $C_2B_{n-2}H_n$ $(5 \le n \le 12)$. Some LCAO–MO calculations by the extended Hückel method on these systems in 1962 shortly after their discovery[5] gave results consistent with the presence of $n + 1$ skeletal bonding orbitals corresponding to $2n + 2$ skeletal bonding electrons in closed polyhedral systems with n vertices and only triangular faces. Subsequent work[6-9] has provided additional evidence for the particularly high stability of closed polyhedral systems with n vertices and $2n + 2$ skeletal electrons. A further development of this more recent work[6,8,9] has been a demonstration of the close analogies between the skeletal bonding in boron cage compounds and that in metal clusters,[10] particularly those of high nuclearity.[11]

This paper presents the first analysis of the bonding topology in these triangulated polyhedral systems using algebraic graph theory.[12] Our new treatment of polyhedral boranes and metal clusters generates directly the $n + 1$ skeletal bonding orbitals in closed polyhedral systems with n vertices. For this reason, we believe that this graph-theoretical analysis will be of considerable value in the further development of the chemistry of these classes of compounds, which are important for applications as diverse as polymeric materials of high thermal stability and catalysts of novel reactivity.

II. Background

The topology of a molecule can be represented by a graph in which the vertices correspond to atoms and the edges to chemical interactions. The topological properties of a molecule as represented by a graph determine the orbital energy scheme and other properties derived from one-electron treatments such as bond orders and charge densities. In many semiempirical theories the topology of the system is sufficient for a satisfactory theoretical treatment of electronic structures, where the integrals, which are not directly determined by the topology, remain as parameters in the equations. Previous workers have shown how topological methods can be used to determine the relative energy levels of various π-electron systems[13,14] and of symmetrical molecules and ions of the type AB_n.[15,16]

Ruedenberg[13] and Schmidtke[15,16] have shown how topological effects can be separated from the usual secular equation

$$|\mathrm{H} - E\mathrm{S}| = 0 \tag{1}$$

by resolving the energy and overlap matrices, respectively, into

$$\mathrm{H} = \alpha\mathbf{I} + \beta\mathbf{A} \tag{2}$$

and

$$\mathbf{S} = \mathbf{I} + S\mathbf{A} \tag{3}$$

where **I** is the unit matrix, α and β are the Hückel Coulomb and resonance integrals, respectively, and **A** is the adjacency matrix of the graph reflecting the topology of the system. The adjacency matrix **A** of a graph,[17] which is commonly used in algebraic graph theory, is defined as follows:

$$\mathbf{A}_{ij} = \begin{cases} 0 \text{ if } i = j \\ 1 \text{ if } i \text{ and } j \text{ are connected by an edge} \\ 0 \text{ if } i \text{ and } j \text{ are not connected by an edge} \end{cases}$$

Substituting eq 2 and 3 into eq 1 leads to the equation

$$|\mathbf{A} - \lambda\mathbf{I}| = 0 \tag{4}$$

where λ corresponds to the energy eigenvalues from the relationship

$$E = \frac{\alpha + \lambda\beta}{1 + \lambda S} \tag{5}$$

This analysis indicates that solution of eq 4 for the eigenvalues λ of the adjacency matrix **A** representing the topology of the system in the molecule under consideration will lead to the Hückel energy levels for the species.

III. Comparison of the Bonding Topology in Closed Polygonal and Polyhedral Species

The analysis of the bonding topology in three-dimensional polyhedra with only triangular faces (hereinafter conveniently known as "deltahedra"[7]) by graph-theoretical methods may be more readily understood if presented in comparison with the bonding topology in benzene (as a familiar example of two-dimensional polygonal systems). Similarly, the bonding topology in the polyhedral systems is more simply analyzed by first considering only the polyhedral boranes and carboranes, thereby limiting the vertex atoms to boron and carbon, which do not use d orbitals for chemical bonding. The demonstrated analogy between polyhedral boranes and carboranes on the one hand and polyhedral metal clusters on the other hand[6,8,9] allows the resulting treatment of the bonding topology in the polyhedral boranes and carboranes to be extended to transition metal cluster systems.

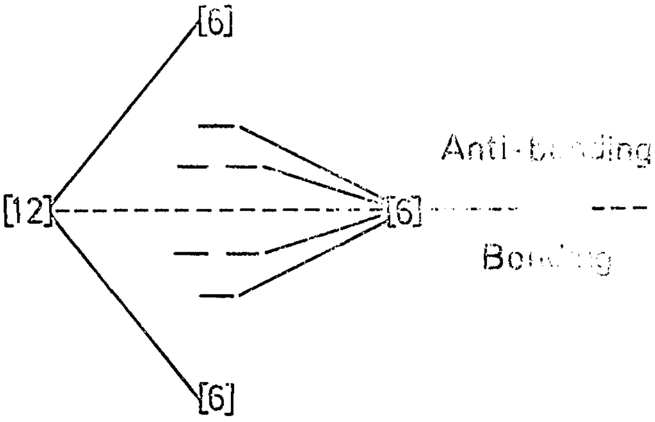

Figure 1. The energy level pattern in benzene (planar hexagon).

In both the polygonal C_nH_n systems and the polyhedral boranes and carboranes with n vertices, the four valence orbitals on each vertex atom may be conveniently divided into one external orbital, two equivalent twin internal orbitals, and one unique internal orbital. External orbitals are used to form one σ bond from each vertex to an external atom or group. Pairwise overlap between the $2n$ twin internal orbitals is responsible for the formation of the polygonal or polyhedral framework of all the vertex atoms and leads to a splitting of the $2n$ orbitals into n bonding and n antibonding orbitals. This is analogous to the generation of equal numbers of bonding and antibonding orbitals in a network consisting of only σ bonding. Global mutual overlap of the n unique internal orbitals on the vertex atoms as determined by the topology of the molecule generates additional bonding and antibonding molecular orbitals with relative energies determined from the eigenvalues λ of the adjacency matrix **A** of the graph representing the topology of the molecule.

Let us first consider the familiar case of benzene. In this polygonal system the external and the two twin internal orbitals are sp^2 hybrids, whereas the unique internal orbital is of p type. The 12 twin internal orbitals interact pairwise to form six bonding and six antibonding orbitals corresponding to the σ bonding and the σ^* antibonding orbitals of the six carbon–carbon σ bonds in the usual molecular orbital treatments.[18] The six unique internal p orbitals interact to give the familiar eigenvalue spectrum[19] of the planar hexagon C_6 consisting of three σ bonding and three σ^* antibonding orbitals. The distribution of the eigenvalues for these interactions is illustrated in Figure 1. In this and subsequent figures a number in brackets, e.g., $[2n]$, refers to the indicated number of degenerate or nondegenerate orbitals at or around the level it is placed.

A completely analogous treatment may be applied to the closed polyhedral boranes and carboranes. The external and unique internal orbitals may now be considered as sp hybrids and the twin internal orbitals as p orbitals. The high observed acidity of carborane C–H hydrogens,[20] which is similar to that in alkynes rather than to that in alkenes or alkanes, provides experimental support for this contention. Pairwise interaction between the $2n$ twin internal orbitals (also known as the *tangential* orbitals[9]) in the surface bonding of the polyhedron leads to n bonding and n antibonding orbitals. Such a pairwise interaction of the $2n$ twin internal orbitals is possible whenever the borane polyhedron contains at least one Hamiltonian circuit. A Hamiltonian circuit of a graph is defined as a cycle (i.e., a connected subgraph with all vertices of degree 2) containing

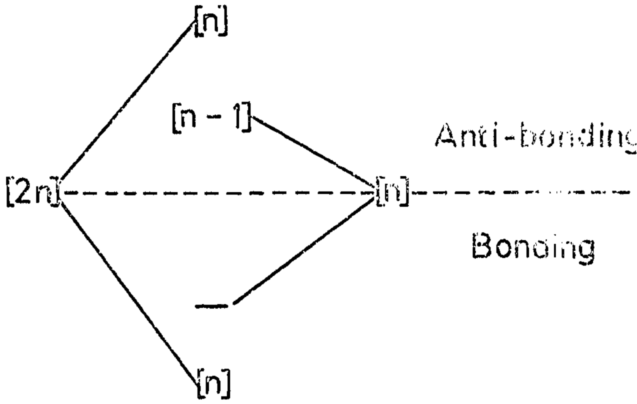

Figure 2. The energy level pattern in a closed polyhedral borane, carborane, or metal cluster having n vertices.

all of the vertices of the graph.[21] All of the deltahedra involved in polyhedral borane and carborane chemistry can readily be shown to contain more than one of the Hamiltonian circuits required for this type of surface bonding of the $2n$ twin internal orbitals. The unique internal orbitals emanating from each vertex of the deltahedron and directed inwards (also known as the radial orbitals[9]) will interact at the center of the deltahedron. As a reasonable first approximation we assume that the pattern of the resulting core bonding may be represented by the complete graph.[22] A complete graph is symbolized as K_n, and every one of its n vertices is connected to every other vertex. The eigenvalue spectrum[23] of K_n for any value of n has only one positive eigenvalue and this is equal to $n - 1$. All of the remaining eigenvalues of K_n are negative and equal to -1. As a consequence it is logical to suppose that the interaction of all the unique internal orbitals in the core bonding of the polyhedron will contribute only one new bonding orbital. The sum of the n bonding orbitals arising from the surface bonding of the twin internal orbitals and the single bonding orbital arising from the n-center core bonding of the unique internal orbitals thereby gives rise to $n + 1$ bonding orbitals for any chemically feasible closed polyhedral cluster on n vertices (Figure 2). Upon filling these bonding orbitals with electron pairs in the usual way, one obtains a total of $2n + 2$ bonding electrons, a result which is in accord with the observed number required to form stable cage boranes and carboranes.[6-9]

Our comparison of the bonding topology in closed polygonal systems such as monocyclic C_nH_n derivatives and closed polyhedral systems such as the dianions $B_nH_n^{2-}$ ($6 \leq n \leq 12$) and the carboranes $C_2B_{n-2}H_n$ ($5 \leq n \leq 12$) demonstrates for the first time the close analogy existing between these polygonal and polyhedral systems. Systems of both types represent species of unusual chemical stability and low reactivity when all of the bonding, but none of the antibonding, molecular orbitals are filled with electron pairs. The *only* significant difference between the algebraic graph-theoretical analysis of the bonding topology in the polygonal and polyhedral systems is in the type of graph used to represent the interactions between the unique internal orbitals of the vertex atoms. These graphs are the cyclic graphs C_n for the polygonal systems and the complete graphs K_n for the polyhedral systems. This seemingly minor difference in the bonding topology of the unique internal orbitals makes a major difference in the form of the relationships between the number of vertices and the number of bonding orbitals.

There are some other interesting points of comparison between the graph-theoretical analysis of the polygonal and polyhedral systems. In graph theory a regular graph is defined as a graph in which all of the vertices are equivalent, i.e., of the same degree. The cyclic graphs C_n involved in the bonding of the unique internal orbitals in the polygonal C_nH_n systems and the complete graphs K_n involved in the bonding of the unique internal orbitals in the polyhedral boranes and carboranes are the *only* general types of regular graphs that are possible for all numbers of vertices. This suggests that no other bonding topology of the unique internal orbitals is possible which leads to globally delocalized systems of a third type fundamentally different from both the polygonal C_nH_n systems and the polyhedral boranes and carboranes. By a liberal adaptation of classical terminology the polygonal C_nH_n systems exemplified by benzene may be regarded as two-dimensional aromatic systems whereas the polyhedral boranes and carboranes may be regarded as three-dimensional aromatic systems. This view is completely in keeping with their observed properties.

A graph-theoretical property of the two-dimensional systems with n vertices (i.e., the polygons) is the presence of only one Hamiltonian circuit for the pairwise overlap of the $2n$ twin internal orbitals in the σ bonding. On the other hand, the three-dimensional systems with n vertices (the deltahedra) contain more than one Hamiltonian circuit for the pairwise overlap of the $2n$ twin internal orbitals in the surface bonding. For this reason the surface bonding of the $2n$ twin internal orbitals in the closed polyhedral boranes and carboranes is more delocalized than the corresponding σ bonding of the $2n$ twin internal orbitals in the polygonal C_nH_n systems, although the general energy level patterns of these analogous types of bonding are fundamentally the same.

IV. Delocalized vs. Localized Bonding in Polyhedral Systems

The graph-theoretical analysis of the bonding topology in polyhedral systems with n vertices leading to $n + 1$ skeletal bonding orbitals and $2n + 2$ skeletal electrons discussed above assumes global delocalization throughout the entire polyhedron. Alternatives to such delocalized polyhedral systems are localized polyhedral systems in which the skeletal bonding consists of simple two-electron σ bonds along each edge of the polyhedron. Such localized polyhedra will have $2k$ skeletal electrons, where k is the number of edges. In general since $2k \neq 2n + 2$ the number of skeletal electrons in a given polyhedral system will determine whether the skeletal bonding is delocalized or localized.

The case of the tetrahedron is particularly interesting and important. Since a tetrahedron has four vertices and six edges, delocalized bonding requires $(2 \times 4) + 2 = 10$ skeletal electrons and localized bonding requires $2 \times 6 = 12$ skeletal electrons. In metal cluster chemistry all tetrahedral systems such as $M_4(CO)_{12}$ (M = Co, Rh, and Ir) have the 12 skeletal electrons required for localized bonding.[8] However, except in unusual cases the clusters based on larger deltahedra such as the octahedron have the appropriate number of skeletal electrons for delocalized bonding.

This anomaly of the tetrahedron in polyhedral systems can arise from its uniqueness in being the only possible polyhedron with all triangular faces *and* with all vertices of degree three. The degree of a vertex is defined as the number of edges meeting at the vertex in question. Localized bonding in a polyhedral system requires hybridization of the vertex atom orbitals such that a hybrid orbital is directed along each edge. The skeletal bonding in polyhedral systems normally involves three internal orbitals from each of the vertex atoms. Among deltahedra, the tetrahedral systems are unique in that three internal orbitals from each of their vertex atoms can participate in edge-localized bonding without any global delocalization. In systems based on larger deltahedra, the presence of vertices of degree four or higher makes localized bonding no longer possible in the normal cases, including the polyhedral boranes and carboranes, where each vertex atom provides only three internal orbitals.

Additional information concerning the circumstances determining whether localization or delocalization occurs may be obtained by examining various six-atom clusters. A delocalized octahedral structure exemplified by compounds such as $Rh_6(CO)_{16}$ (ref 24), $Co_6(CO)_{15}^{2-}$ (ref 25), $H_2Ru_6(CO)_{18}$ (ref 26), and $Ru_6(CO)_{17}C$ (ref 27) requires three internal orbitals from each vertex and 14 skeletal electrons. A localized octahedron requires four internal orbitals from each vertex and 24 skeletal electrons. In systems such as the cobalt, rhodium, and ruthenium carbonyl derivatives listed above, which contain only heavy vertex atoms with available electron pairs, a localized octahedron will require two less skeletal electrons than a delocalized octahedron.

The more severe requirement of the localized octahedron is the requirement of four internal orbitals from each vertex rather than the three internal orbitals from each vertex required for the delocalized polyhedra including the delocalized octahedron. The required four internal orbitals for a vertex atom in a *localized* polyhedron with vertices of degree four must be directed onto one side of a supporting plane[28,29] of the polyhedron. Alternatively stated, these four internal orbitals must all be located in the same hemisphere of the coordination sphere. In the frequently adopted octahedral hybridization for the vertex atoms in metal carbonyl systems, etc., this arrangement is not possible without considerable angular strain since among any four of the six octahedral sp^3d^2 hybrids, the angles between at least two must be 180°. Possible hybridizations for atoms at vertices of degree four in localized polyhedra lead to the square pyramid, the trigonal prism, and various configurations for coordination numbers seven, eight, and nine. The orbitals provided by such hybridizations include four possible internal orbitals directed on one side of a supporting plane. Light vertex atoms such as boron and carbon, which use only s and p orbitals for bonding, clearly can never be found at vertices of degree four or higher in *localized* polyhedra.

Several examples of octahedral clusters are known in which the number of skeletal electrons indicates localized skeletal bonding rather than the usual delocalized skeletal bonding discussed above. None of the vertex atoms in any of these localized octahedra are the light atoms boron or carbon which do not use d orbitals for chemical bonding. One category of localized octahedral clusters includes the cobalt complexes $Co_4(CO)_{10}S_2$ and $Co_4(CO)_{10}(PR)_2$ in which phosphorus or sulfur atoms occupy two of the vertices of the octahedron. In these clusters the hybridization of the phosphorus or sulfur atoms is based on a square pyramid and the hybridization of the cobalt atoms is based on a relatively unsymmetrical seven-coordinate polyhedron. The extensive series of compounds of the types[31] $[(Mo_6Cl_8)X_6]^{2-}$ and $[(Mo_6Cl_8)L_6]^{4+}$ (X and L = one- and two-electron donor ligands, respectively) are also based on localized octahedra. In these systems each vertex molybdenum atom is nine-coordinate, which allows four of the resulting hybrid orbitals to be used as internal orbitals for the edge bonding of the localized octahedron.

The trigonal prism is an example of a six-vertex polyhedron in which all vertices have degree three. In this latter respect the trigonal prism resembles the tetrahedron. The known trigonal prismatic complexes are the carbides $[M_6(CO)_{15}C]^{2-}$ (M = Co[32] and Rh[33]), in which the central carbon atom appears to expand the six-metal cluster from the octahedron to the more voluminous trigonal prism, which has three rectangular faces. If each vertex metal atom in the trigonal prismatic $[M_6(CO)_{15}C]^{2-}$ clusters contributes three orbitals to the trigonal prism, these systems can obtain six skeletal electrons from the six $M(CO)_2$ units, six skeletal electrons from the "extra" three CO groups, four skeletal electrons from the core carbon atom, and two skeletal electrons from the −2 net charge to give a total of 18 skeletal electrons. This corresponds to localized bonding along each edge of the nine edges of the trigonal prism. The localized bonding in these trigonal prismatic clusters provides further evidence that the degree 3 for all vertices of the tetrahedron is responsible for the apparent universal preference of tetrahedral metal clusters for localized over delocalized bonding in contrast to clusters based on larger deltahedra which prefer delocalized bonding except in unusual cases such as those cited above.

V. Electron-Rich and Electron-Poor Polyhedral Clusters

The graph-theoretical analysis of the bonding topology in closed globally delocalized deltahedral systems with n vertices discussed above indicates the presence of $n + 1$ skeletal bonding orbitals. This agrees with experimental observations on the stability of such systems when they contain $2n + 2$ skeletal electrons. We now examine the properties of both electron-rich polyhedral systems containing more than $2n + 2$ skeletal electrons and electron-poor polyhedral systems containing less than $2n + 2$ skeletal electrons in order to determine the applicability of our methods to the analysis of the bonding topologies in such systems.

The electron-rich polyhedral systems have already been discussed in some detail in the literature, particularly in the case of boron hydride derivatives.[7] There are now well-established families of nido compounds with $2n + 4$ skeletal electrons and of arachno compounds with $2n + 6$ skeletal electrons. If only triangular faces are considered as closed in accord with previous treatments,[29] then the nido compounds contain one hole or nontriangular face. The arachno compounds contain either two holes or one large bent hole. Thus successive additions of electron pairs to a closed $2n + 2$ deltahedron result in successive punctures of the deltahedral surface to give holes with more than three edges by a process conveniently called *polyhedral puncture*. Alternatively stated, the open polyhedral networks can arise from excision of one or more vertices along with all of the edges leading to them from a closed deltahedron with a larger number of vertices by a process conveniently called *polyhedral excision*.

We shall now consider the nido systems in order to illustrate the applicability of our method for the graph-theoretical analysis of bonding topology to electron-rich polyhedral systems. The vertex atoms of the nido polyhedron may be divided into the following two sets: border vertex atoms which are vertices of the one face containing more than three edges (i.e., they are at the border of the single hole) and interior vertex atoms which form vertices of triangular faces only. For example, in a square pyramid, which is the simplest example of a nido polyhedron, the four basal vertices are the border vertices since they all border the square "hole". However, the single apical vertex of a square pyramid is an interior vertex since it is a vertex of only triangular faces. The external and twin internal orbitals of the border vertex atoms are taken to be sp^2 hybrids in accord with the observed[34] C–H coupling constant of 160 Hz for the border vertex carbon atom in the nido-carborane $C_2B_4H_8$. The unique internal orbitals of the border vertex atoms will thus be p orbitals. The external and unique internal orbitals of the interior vertex atoms are taken to be sp hybrids in accord with the treatment of closed deltahedra discussed above. The twin internal orbitals of the interior vertex atoms must therefore be p orbitals.

We shall now consider the bonding topology of the internal orbitals of the vertex atoms of nido polyhedra having a total of n vertices, of which v are interior vertices ($v > 1$). The interactions between the internal orbitals in nido systems which generate bonding orbitals are of the following three different types and lead to the energy levels depicted in Figure 3:

(a) The $2(n - v)$ twin internal orbitals of the border atoms and the $2v$ twin internal orbitals of the interior atoms interact

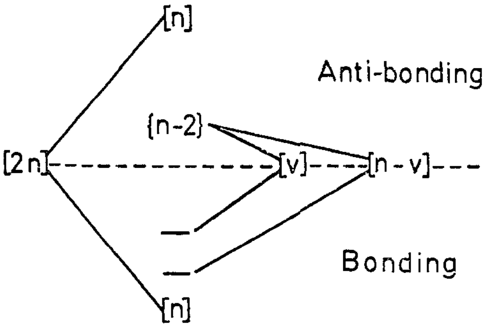

Figure 3. The energy level pattern in a nido polyhedral cluster with n vertices and v interior vertices ($v > 1$). The detailed pattern of the $n - 2$ antibonding orbitals is immaterial.

along the polyhedral surface to form n bonding orbitals and n antibonding orbitals.

(b) The v unique internal orbitals of the interior vertex atoms all interact with each other at the core of the structure in a way which may be represented by the complete graph K_v to give a single bonding orbital and $v - 1$ antibonding orbitals.

(c) The $n - v$ unique internal orbitals of the border atoms interact with each other across the surface of the hole in a way which may be represented by the complete graph K_{n-v} to give a single bonding orbital and $n - v - 1$ antibonding orbitals.

The above interactions in nido systems of types a and b correspond to the interactions found in the closed deltahedral systems discussed above whereas the interaction of type c can only occur in polyhedra containing at least one hole such as the nido systems. Furthermore, in the interactions of types b and c above, the values of v and $n - v$ are immaterial as long as they both are greater than one, since any complete graph K_i ($i > 1$) has exactly one positive eigenvalue, nanely, $i - 1$. The total number of skeletal bonding orbitals in nido systems with n vertices generated by interactions of the types a, b, and c are n, 1, and 1, respectively, leading to a total of $n + 2$ bonding orbitals holding $2n + 4$ skeletal electrons. This is accord with experimental observations.[7]

The process of polyhedral puncture which forms nido polyhedra with one hole and $2n + 4$ skeletal electrons from closed deltahedra with $2n + 2$ skeletal electrons can be continued further to give polyhedral fragments with two or more holes. Each time a new hole is added by such polyhedral puncture, the complete graph formed by type b interactions at the polyhedral core between the unique internal orbitals of the interior vertex atoms is split into two new complete graphs. One of these new complete graphs involves a type b interaction at the polyhedral core between the unique internal orbitals of the vertex atoms which are still interior atoms after creation of the new hole. The second new complete graph involves a type c interaction over the newly created hole between the unique internal orbitals of the vertex atoms which have become border atoms of the newly created hole. Since each new complete graph contributes exactly one skeletal bonding orbital to the polyhedral system, each application of polyhedral puncture to give a stable system requires addition of two electrons. A real chemical example of polyhedral puncture is the addition of two electrons to the closed icosahedral carborane o-$C_2B_{10}H_{12}$ to give the nido dianion $C_2B_{10}H_{12}^{2-}$ containing a hexagonal hole.[35] A suitable reagent for effecting this chemical transformation is sodium metal in the presence of naphthalene; not surprisingly, this reagent is an excellent source of electrons.

The properties of electron-poor (also called electron-hyperdeficient[36]) polyhedral systems containing less than $2n + 2$ skeletal electrons have been discussed in less detail, apparently because representatives of this class of compounds are much rarer. Actually, the structural characteristics of electron-poor polyhedra can be most readily derived by examining a seemingly unrelated question: why are some closed deltahedra found in closed boron hydride and carborane structures and others not?

Table I lists some closed deltahedra with 4–12 vertices. For the deltahedra containing 7, 8, 10, and 11 vertices two alternative closed deltahedra containing different symmetry elements are listed. In each of these cases one of the deltahedra is found in deltahedral boranes and carboranes and the other is not. In all four cases the unfavorable deltahedra with n vertices can be partitioned into a tetrahedron and a smaller closed deltahedron with $n - 1$ vertices by using only edges present in the larger deltahedron. In this partition the tetrahedron and the deltahedron with $n - 1$ vertices have one face in common. Thus the bicapped octahedron with 8 vertices can be partitioned into a tetrahedron and a capped octahedron with 7 vertices; the capped octahedron with 7 vertices in turn can be partitioned into a tetrahedron and a octahedron with 6 vertices. Similarly, the pentacapped trigonal prism with 11 vertices can be partitioned into a tetrahedron and a 3,4,4,4-tetracapped trigonal prism with 10 vertices, which in turn can be partitioned further into another tetrahedron and a 4,4,4-tricapped trigonal prism with 9 vertices. Further tetrahedra cannot be removed analogously from either the octahedron or the 4,4,4-tricapped trigonal prism. These deltahedra which can be partitioned into a tetrahedron and a smaller deltahedron can also be visualized as containing one or more capped triangular faces. Furthermore, this type of deltahedral partitioning by "casting out tetrahedra" requires a vertex of degree three. The deltahedra which cannot be so partitioned contain no vertex of degree three: all of their vertices are of degree four or higher.

A feature of the tetrahedron discussed above which is unique for closed deltahedra is the stability of systems containing the 12 skeletal electrons indicative of localized bonding along the six edges. Analogy with the isolated tetrahedron suggests that bonding within a tetrahedral chamber of a polyhedron containing a capped triangular face will also be similarly localized. For convenience, such deltahedra based on smaller deltahedra with one or more capped faces will be called "capped deltahedra".

In the polyhedral boranes and carboranes the vertex atoms have only four orbitals. One of these orbitals is used to bond to the external substituent. This leaves exactly three orbitals to participate in the delocalization in the deltahedron which, as discussed above, leads to $n + 1$ bonding orbitals which can accommodate $2n + 2$ skeletal bonding electrons. If, however, a face of the deltahedron is capped, then four orbitals from the vertex atoms of the capped face are needed for the cluster bonding: three for the delocalized bonding in the central deltahedron and a fourth orbital for the localized bond to the cap. However, boron and carbon have a total of only four bonding orbitals since they use only s and p orbitals for chemical bonding. These four bonding orbitals cannot all be directed inward toward the cluster polyhedron without introducing excessive strain. This prevents light vertex atoms such as boron and carbon from occurring at vertices of capped triangular faces (at least in isolated polyhedra such as those discussed in this paper). This excludes capped deltahedra such as the capped and bicapped octahedra and the 3,4,4,4-tetracapped and pentacapped trigonal prisms from polyhedral boranes and carboranes in which the only vertex atoms are boron and carbon.

Transition metals forming clusters, unlike boron and carbon, have up to nine bonding orbitals rather than only four since they use d orbitals as well as s and p orbitals for chemical bonding. Transition metals can thus appear as vertices of capped triangular faces. Two examples of capped transition metal clusters are the osmium carbonyl $Os_6(CO)_{18}$ based on a bicapped tetrahedron[37] and the rhodium carbonyl anion

Table I. Some Deltahedra

Deltahedron	Point group	No. of elements[a]			Types of vertices[a]				Found in metal-free borane and carborane polyhedra	Found in metalloboranes and metal clusters
		v	e	t	j_3	j_4	j_5	j_6		
Tetrahedron	T_d	4	6	4	4	0	0	0	No[b]	Yes
Trigonal bipyramid	D_{3h}	5	9	6	2	3	0	0	Yes	Yes
Octahedron	O_h	6	12	8	0	6	0	0	Yes	Yes
Pentagonal bipyramid	D_{5h}	7	15	10	0	5	2	0	Yes	Yes
Capped octahedron	C_{3v}	7	15	10	1	3	3	0	No	Yes
D_{2d} "dodecahedron"	D_{2d}	8	18	12	0	4	4	0	Yes	Yes
Bicapped octahedron	D_{3d}	8	18	12	2	0	6	0	No	No
4,4,4-Tricapped trigonal prism	D_{3h}	9	21	14	0	3	6	0	Yes	Yes
4,4-Bicapped square antiprism	D_{4d}	10	24	16	0	2	8	0	Yes	Yes
3,4,4,4-Tetracapped trigonal prism	C_{3v}	10	24	16	1	3	3	3	No	Yes
$B_{11}H_{11}^{2-}$ polyhedron	C_{2v}	11	27	18	0	2	8	1	Yes	Yes
Pentacapped trigonal prism	D_{3h}	11	27	18	2	3	0	6	No	No
Icosahedron	I_h	12	30	20	0	0	12	0	Yes	Yes

[a] v refers to the number of vertices, e refers to the number of edges, t refers to the number of triangular faces, j_n refers to the number of vertices of degree n. See R. B. King, *J. Am. Chem. Soc.*, **91,** 7211 (1969). [b] B_4Cl_4 is an example of a boron tetrahedron. However, B_4Cl_4 does not have the high chemical stability characteristic of the polyhedral boranes.

$Rh_7(CO)_{16}^{3-}$ based on a capped octahedron.[38] In both of these transition metal clusters, unlike the cage carboranes and boranes, there is considerable bonding flexibility depending upon whether vertex metal electron pairs are involved in the cluster bonding or appear as lone pairs. In other words, the analogy between transition metals on the one hand and boron and carbon on the other hand as vertex atoms in polyhedral clusters[6] breaks down when capped deltahedra are considered since such polyhedra require some vertex atoms which can contribute four or more internal orbitals to the skeletal bonding.

Examination of the capped transition metal clusters $Os_6(CO)_{18}$ and $Rh_7(CO)_{16}^{3-}$ indicates that the bonding in capped deltahedra can be understood if the cap contributes the same number of electrons to the central polyhedron as if it were a vertex of the central polyhedron. However, since the cap pariticpates only in localized bonding and is located above the surface of the central polyhedron, it does not contribute any new internal orbitals to affect the delocalization of the central polyhedron. Capping is therefore a good mechanism to contribute electrons to a central polyhedron without contributing any new bonding orbitals. It is thus a good remedy for electron poverty. Indeed, both $Os_6(CO)_{18}$ and $Rh_7(CO)_{16}^{3-}$ are electron-poor clusters containing $2n$ rather than $2n + 2$ skeletal electrons.

An even simpler example of a capped deltahedron is the trigonal bipyramid, which can be considered as a capped tetrahedron. Both the tetrahedron and the trigonal bipyramid require 12 skeletal electrons for stability. This is consistent with the idea that in the trigonal bipyramid the cap, which is one of the two apices (i.e., vertices of degree 3), contributes the usual number of skeletal electrons but no new bonding orbitals.

Recently some rather exotic electron-poor polyhedral metalloboranes and metallocarboranes have been characterized structurally which provide some interesting tests and extensions of these general principles. The complex[39] $(C_5H_5)_3Co_3B_4H_4$ is a $2n$ skeletal electron system which appears from its ^{11}B NMR spectrum to be a monocapped octahedron with a BH group capping the triangular face containing three cobalt atoms as vertices. Thus, this compound obeys the requirement of transition metals rather than light boron or carbon atoms at all vertices of capped triangular faces. The complex[40] $(C_5H_5)_2Fe_2C_2B_6H_8$ appears to be an electron-poor 3,4,4,4-tetracapped trigonal prism (Table I) in which the C_5H_5Fe, BH, and CH vertices contribute 1, 2, and 3 skeletal electrons, respectively, thereby resulting in $2 \times 1 + 6 \times 2 + 2 \times 3 = 20 = 2n$ skeletal electrons for this ten-vertex system. However, in this system an additional two electrons otherwise required for an iron–iron bond can also function as skeletal electrons because of the location of the iron atoms relative to the polyhedron. This makes $(C_5H_5)_2Fe_2C_2B_6H_8$ a favored $2n + 2$ skeletal electron 4,4-bicapped square antiprism (Table I) with the distortion necessary to accommodate the iron–iron bond involving the iron atoms located at otherwise nonadjacent vertices of the polyhedron. The complex[36] $(CH_3)_4C_4B_8H_8FeCoC_5H_5$, which contains two pentagonal bipyramids with one vertex in common (the iron atom) as well as an "extra" BH group joined to the iron atom and to both pentagonal bipyramids, involves additional principles clearly beyond the treatment of this paper. However, if the CH_3C, BH, and C_5H_5Co vertices contribute the usual 3, 2, and 2 skeletal electrons, respectively, then each pentagonal bipyramid can have the favored $2n + 2$ (i.e., 16) skeletal electrons if it receives an additional two skeletal electrons from the central iron atom.

The analysis in this paper indicates that there are two opposite or dual processes for converting closed deltahedra with n vertices which require $2n + 2$ skeletal electrons into polyhedra appropriate for systems with a larger or smaller number of skeletal electrons relative to the number of vertices. For electron-rich systems with more than $2n + 2$ electrons the appropriate process is polyhedral excision or the equivalent polyhedral puncture as discussed above. In polyhedral excision a vertex and all of its incident edges are removed so that more electrons than bonding orbitals are lost. For electron-poor systems with less than $2n + 2$ skeletal electrons the appropriate process is polyhedral capping in which a triangular face is capped with a new vertex to add electrons to the system without adding bonding orbitals.

Deviations from the favored $2n + 2$ skeletal electrons for polyhedral systems either by forming electron-rich systems through successive punctures or electron-poor systems through successive capping lead to increased bonding localization. Each polyhedral puncture splits the single multicenter bonding molecular orbital formed by the overlap of the unique internal orbitals of the interior vertex atoms at the core of the polyhedron (type b above) into two new bonding molecular orbitals, one still at the core (type b) and one above the newly created hole (type c). This results in an increasing localization of the system. Similarly, adding each cap increases the portion of the cluster that is contained in the localized tetrahedral chambers rather than in the delocalized larger central polyhedra. Thus repeated punctures or cappings will lead to more highly localized systems that may lose many of the interesting properties, including the relatively high chemical stability, that are characteristic of many of the closed deltahedral clusters containing $2n + 2$ skeletal electrons.

VI. Conclusions

Our graph-theoretical analysis of the bonding topology in three-dimensional closed deltahedral systems such as the cage boranes and carboranes has indicated for the first time the close relationship existing between the delocalization in the three-dimensional polyhedral systems with n vertices and $2n + 2$ skeletal electrons on the one hand and the delocalization in two-dimensional polygonal systems with $4k + 2$ (k positive integral) π electrons on the other hand. However, a similar type of delocalization never appears to occur in tetrahedral clusters where in all presently known systems the bonding can be explained in terms of localized bonding along the six edges. The degree three for all vertices of a tetrahedron appears to be the key factor in making such edge-localized bonding universal. The graph-theoretical analysis of bonding topology can also be applied to the electron-rich nido systems with one hole, n vertices, and $2n + 4$ skeletal electrons as well as to less delocalized systems with even more skeletal electrons and holes. Electron-poor cluster systems with n vertices and less than $2n + 2$ skeletal electrons form polyhedra with one or more capped triangular faces. However, such electron-poor cluster systems appear to require transition metals at the vertices of the faces being capped and therefore are not feasible for cage carboranes and boranes with only boron and carbon as vertex atoms. Puncture or excision of closed deltahedra to form open polyhedra with one or more holes which are appropriate for electron-rich systems with more than $2n + 2$ skeletal electrons may be considered as opposite or dual to the capping of closed deltahedra to form larger deltahedra with tetrahedral chambers which are appropriate for electron-poor systems with less than $2n + 2$ skeletal electrons.

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