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Chemical Applications of Topology and Group Theory.
11. Degenerate Edges as a Source of Inherent Fluxionality in Deltahedra*

R. BRUCE KING
Department of Chemistry, University of Georgia, Athens, Ga. 30602, U.S.A.

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The 5, 8, 9, and 11 vertex deltahedra containing the minimum number of tetrahedral chambers are inherently fluxional since certain possible diamond-square-diamond rearrangements can lead directly to a polyhedron identical to the original one except for interchanges of some vertices. By this criterion the 6, 10, and 12 vertex deltahedra are inherently rigid. The 7 vertex pentagonal bipyramid is also inherently rigid but can be stereochemically non-rigid in cases where a capped octahedron is an accessible intermediate. These topological observations are consistent with known information on the stereochemical non-rigidity and hydrolytic stability of the deltahedral borane anions $B_nH_n^{2-}$ *and the stereochemical non-rigidity of* ML_n *coordination complexes. Thus the stereochemical non-rigidity of all* ML_7 *complexes investigated as contrasted with the stereochemical rigidity of* $B_7H_7^{2-}$ *can be related to the energetic accessibility of capped octahedral species in* ML_7 *complexes but not in* $B_7H_7^{2-}$*.*

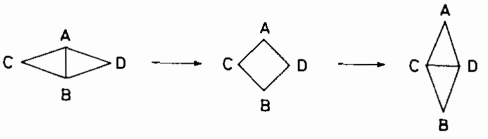
Introduction

The extensive development of the chemistry and spectroscopy of stereochemically non-rigid [2–4] or fluxional [5] molecules has stimulated theoretical treatments of such systems using a variety of approaches. Thus topological representations [6, 7] of polyhedral rearrangements have been developed for coordination complexes of the type ML_n (M = central atom, most frequently a metal; L = ligands; n = four [6], five [8], six [9] and eight [1]). The stereochemical non-rigidity of ML_n complexes has also been related to mismatching of the spectra of the L_n graphs with the available bonding orbitals of M [10].

This paper relates a simple and purely topological property of polyhedra having only triangular faces (deltahedra) to their propensity to form fluxional systems. In this treatment no assumptions are necessary concerning relative energies of atomic orbitals or other chemical parameters. Deltahedral chemical species to which this treatment can be applied include boranes, carboranes, and ML_n coordination complexes.

Degenerate Edges of Deltahedra

The major assumption of this treatment is that the lowest energy processes for polyhedral rearrangements can be decomposed into one or more diamond-square-diamond (dsd) processes [11]. Such a dsd-process in a deltahedron occurs at two (triangular) faces sharing an edge and can be depicted schematically as follows:



Ia Ib Ic

In this process a configuration such as Ia can be called a *dsd-situation* and the edge AB can be called a *switching edge*. If a, b, c, and d are taken to represent the degrees of the vertices A, B, C, and D, respectively (*i.e.*, the total number of edges meeting at the vertex in question), then the *dsd-type* of the switching edge AB can be represented as ab(cd). In this designation, the first two digits refer to the degrees of the vertices joined by AB and the two digits in parentheses refer to the degrees of the two vertices not joined by AB but contained in the faces (triangles) having AB as the common edge.

A deltahedron with e edges has e distinct dsd-situations, one corresponding to each of the e edges acting as the switching edge. Applications of the dsd-process at each of the dsd-situations in a given deltahedron will in each case lead to a new deltahedron. In most cases the new deltahedron will be relatively unsymmetrical and also may have vertices of degree 3 leading to tetrahedral chambers which are

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*See Ref. 1.

TABLE I. Properties of the Edges of Some Deltahedra.

Deltahedron[a]	No. of elements[b]				Number	Types of Edges		Square Intermediate[d]
	v	e	f	j_3		dsd Type[c]	Degenerate	
Tetrahedron	4	6	4	4	6	33(33)	No	–
Trigonal Bipyramid	5	9	5	2	6	34(44)	No	–
					3	44(33)	Yes	Square Pyramid (1)
Octahedron	6	12	8	0	12	44(44)	No	–
Pentagonal Bipyramid	7	15	10	0	5	44(55)	No	–
					10	45(44)	No[e]	
D_{2d}-Dodecahedron	8	18	12	0	2	44(55)	No	–
					8	45(45)	No	–
					4	45(55)	No	–
					4	55(44)	Yes	Square Antiprism (2)
D_{3h}-Tricapped Trigonal Prism	9	21	14	0	12	45(55)	No	–
					3	55(44)	Yes	Capped Square Antiprism (1)
					6	55(45)	No	–
D_{4d}-Bicapped Square Antiprism	10	24	16	0	8	45(55)	No	–
					8	55(45)	No	–
					8	55(55)	No	–
$B_{11}H_{11}^{2-}$ Polyhedron[f]	11	27	18	0	2	45(55)	No	–
					4	45(56)	No	–
					2	46(55)	No	–
					4	55(45)	No	–
					9	55(55)	No	–
					2	55(56)	No	–
					4	56(45)	Yes	11,26,17-Polyhedron (1)
Icosahedron	12	30	20	0	30	55(55)	No	–

[a] If more than one deltahedron for a given number of vertices are possible, the deltahedron with a minimum number of tetrahedral chambers is considered.

[b] v = number of vertices; e = number of edges; f = number of faces; j_3 = number of vertices of degree 3 (*i.e.* number of tetrahedral chambers for deltahedra other than the tetrahedron itself); note that v + f = e + 2 by Euler's relationship and 2e = 3f because of the presence of only triangular faces (see R. B. King, *J. Am. Chem. Soc.*, *91*, 7211 (1969)).

[c] See text for a definition of this terminology.

[d] This indicates the square intermediate involved in a dsd-process using this type of edge. The number in parentheses corresponds to the number of suitable dsd-processes using this type of edge which are necessary to give the indicated polyhedron.

[e] A dsd-process using edges of this type gives a capped octahedron.

[f] For a picture of this polyhedron see Fig. 5 of F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, *5*, 1955 (1966).

unfavorable in polyhedral boranes and carboranes for reasons discussed elsewhere [12]. However, in some cases the new deltahedron will be identical to the original deltahedron. In these cases the switching edge can be said to be *degenerate.* A dsd-process involving a degenerate switching edge represents a pathway for a fluxional process of the deltahedron. Thus deltahedra containing one or more degenerate edges are inherently fluxional whereas deltahedra without degenerate edges are inherently rigid.

The dsd-type of a degenerate edge ab(cd) can be seen by application of the process Ia → Ib → Ic to satisfy the following conditions:

$$c = a - 1 \text{ and } d = b - 1 \text{ or } c = b - 1 \text{ and } d = a - 1$$

Using these conditions the chemically significant deltahedra can be checked for the presence of one or more degenerate edges (Table I) with the following results:

(A) Tetrahedron: No dsd-process is possible since all six pairs of vertices already have edges between them (*i.e.*, a tetrahedron is a complete graph [13], namely K_4). A tetrahedron is therefore inherently rigid.

(B) Trigonal Bipyramid: The three edges connecting pairs of equatorial vertices are degenerate. A dsd-process using one of these degenerate edges as the switching edge corresponds to the Berry pseudorotation [14, 15] which is believed to be the mechanism responsible for the stereochemical non-rigidity of trigonal bipyramidal five-coordinate complexes, even at relatively low temperatures [15, 16]. The dsd-process using a 44(33) edge of the trigonal bipyramid involves a square pyramid intermediate.

(C) Octahedron: The highly symmetrical octahedron has no degenerate edges. Fluxional processes in octahedral complexes are therefore necessarily of high energy and in fact are only observable when

the octahedron is highly distorted such as in *cis*-$[(CH_3)_3Si]_2Fe(CO)_4$ (ref. 17).

(D) Pentagonal Bipyramid: The pentagonal bipyramid has no degenerate edges and thus by definition is inherently rigid. However, a dsd-process using a 45(44) edge of the pentagonal bipyramid (namely the edge connecting an equatorial vertex with an apical vertex) will give a capped octahedron. The capped octahedron is a low energy polyhedron for ML_7 coordination complexes [18] but a forbidden polyhedron for carboranes and boranes because of its tetrahedral chamber [12]. This suggests that ML_7 complexes will be fluxional but that pentagonal bipyramidal boranes and carboranes will not be fluxional.

(E) D_{2d}-Dodecahedron: The D_{2d}-dodecahedron has four pairwise degenerate edges, which are those of the type 55(44) located in the subtetrahedron consisting of the degree 5 vertices of the D_{2d}-dodecahedron. Thus two successive or more likely concerted dsd-processes involving opposite 55(44) edges (*i.e.*, a pair related by a C_2 symmetry operation) will convert one D_{2d}-dodecahedron into another through a D_{4d}-square antiprismatic intermediate. This process is described in detail in the previous paper of this series (Fig. 3C in reference 1). Fluxional processes in eight-vertex systems clearly have low energies.

(F) *D_{3h}-Tricapped Trigonal Prism*: The three edges of the type 55(44) corresponding to the "vertical" edges of the trigonal prism are degenerate. A dsd-process using one of these degenerate edges as the switching edge involves a C_{4v} capped square antiprism intermediate and was described several years ago [19]. Nine-vertex systems are therefore inherently fluxional.

(G) D_{4d}-Bicapped Square Antiprism: This polyhedron has no degenerate edges. Ten-vertex systems are therefore inherently rigid.

(H) C_{2v}-$B_{11}H_{11}^{2-}$ Polyhedron [20]: The four edges of the type 56(45) are degenerate. This eleven-vertex deltahedron is therefore inherently fluxional.

(I) Icosahedron: This highly symmetrical polyhedron, like the octahedron, has no degenerate edges and is therefore inherently rigid.

Chemical Implications

This analysis indicates that in deltahedral species the 4, 6, 10 and 12 vertex systems are inherently rigid and the 5, 8, 9 and 11 vertex systems are inherently fluxional. Furthermore, fluxionality in 7 vertex systems requires both the pentagonal bipyramid and the capped octahedron to be low energy species. These observations relate to some known chemistry of deltahedral species in the following ways:

(A) Deltahedral Borane Anion Fluxionality: Among the deltahedral borane anions $B_nH_n^{2-}$ the following observations have been made [21]:

(a) the 5 vertex system $B_5H_5^{2-}$ is unknown apparently since its trigonal bipyramid would consist of two tetrahedral chambers fused at a face, a situation forbidden in polyhedral borane chemistry [12].

(b) the 8 and 11 vertex systems are fluxional on the ^{11}B NMR time scale.

(c) the 6, 7, 9, 10 and 12 vertex systems are rigid on the ^{11}B NMR time scale. The fluxionality of the 8 and 11 vertex $B_nH_n^{2-}$ species and the rigidity of the 6, 10, and 12 vertex $B_nH_n^{2-}$ species all agree with the observations of the inherent fluxionality or rigidity of the corresponding deltahedra (see above). In the 7 vertex system the tetrahedral chamber in the required capped octahedral intermediate makes its energy too high for fluxional processes to occur in the pentagonal bipyramidal $B_7H_7^{2-}$.

The rigidity of the 9 vertex $B_9H_9^{2-}$ system is the most difficult to explain in view of the inherent fluxionality of its deltahedron, the D_{3h}-tricapped trigonal prism. However, the necessary C_{4v} capped square antiprismatic intermediate has a four-fold principal rotation axis in contrast to the three-fold principal rotation axis in the D_{3h} tricapped trigonal prism. This may make the 9 vertex C_{4v} intermediate of relatively high energy compared with the corresponding 'square' intermediates in the dsd-processes in the fluxional 8 and 11 vertex $B_nH_n^{2-}$ systems. This is consistent with some reported [19] calculations on 9 vertex polyhedra.

(B) Deltahedral Borane Anion Hydrolytic Stability: An observation in the "coordination number pattern recognition" theory [22] is that BH groups prefer vertices of degree 5 over those of degree 4. If this is the only factor affecting deltahedral borane hydrolytic stability, then as n increases from 6 to 12, the stability of the corresponding $B_nH_n^{2-}$ system should increase monotonically as more BH groups appear at vertices of degree 5 rather than degree 4. However, there are some significant deviations from such a monotonic hydrolytic stability sequence since the actual [23] hydrolytic stabilities of the $B_nH_n^{2-}$ anions increase in the following sequences of values of n:

$$7 \text{ (least)} < 6 \sim 8 \sim 9 < 10 \sim 11 < 12 \text{ (greatest)}.$$

The most glaring anomaly in this hydrolytic stability sequence is the abnormally small hydrolytic stability of the pentagonal bipyramidal $B_7H_7^{2-}$. However, as noted above a dsd-process on a 45(44) edge of pentagonal bipyramidal $B_7H_7^{2-}$ leads to a capped octahedron. The BH group at the degree 3 vertex in the localized tetrahedral chamber [12] of this capped octahedron should be much more easily attacked by water than the BH group at the vertices of degree 4 or greater which are the only type found in the stable deltahedra lacking tetrahedral chambers.

The hydrolytic stabilities of the 8, 9, and 11 vertex $B_nH_n^{2-}$ anions, which involve inherently fluxional polyhedra, are low relative to those of the 6, 10, and 12 vertex $B_nH_n^{2-}$ anions which involve inherently rigid polyhedra after allowing for the monotonic increase in $B_nH_n^{2-}$ hydrolytic stabilities as n increases from 6 to 12 expected on the degrees of the BH vertices alone. This suggests that other things being equal inherently fluxional deltahedral species will be more chemically reactive than inherently rigid deltahedral species.

(C) Fluxionality of ML_n Coordination Complexes: The number of known ML_n coordination complexes is certainly several orders of magnitude greater than the number of known polyhedral boranes. However, the range of comparison of experiment to theory is more limited in ML_n compounds than in $B_nH_n^{2-}$ species since in ML_n compounds, the maximum value of n is 9 for covalently bonded compounds of substitutionally inert M (*i.e.*, 1s + 3p + 5d = 9 valence orbitals of M). Nevertheless, the available information indicates that the tendency of ML_n compounds to form stereochemically non-rigid systems relates to the inherent fluxionality of the corresponding L_n polyhedron. Thus ML_4 and ML_6 systems based on the inherently rigid tetrahedron and octahedron, respectively, are invariably rigid on the NMR time scale. In the case of ML_7 complexes the pentagonal bipyramid and capped octahedron have roughly comparable energies [18] in contrast to the deltahedral boranes and carboranes where only the pentagonal bipyramid is found. Therefore ML_7 complexes are inherently fluxional in accord with the experimentally observed fluxionality on the NMR time scale in IF_7 (ref. 24), ReF_7 (ref. 25), and $[(Me_3CNC)_7Mo][PF_6]_2$ (ref. 26). The remaining accessible ML_n coordination polyhedra (n = 5, 8, and 9) are inherently fluxional in accord with the experimentally observed fluxionality on the NMR time scale in five-coordinate complexes [15] such as $Fe(CO)_5$ (ref. 27) and PF_5 (ref. 28), in eight-coordinate complexes [29] such as $Mo(CN)_8^{4-}$ (ref. 30), and in the nine-coordinate complex ReH_9^{2-} (ref. 31).

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