Chemical applications of topology and group theory
15. Representations of polyhedral isomerizations using Gale diagrams*

R. Bruce King

Department of Chemistry, University of Georgia, Athens, Georgia 30602, USA

Polyhedral isomerizations of the type $P_1 \rightarrow P_2 \rightarrow P_3$ are degenerate if $P_1$ is combinatorically equivalent to $P_3$ and planar if $P_2$ is a planar polygon. This paper systematizes degenerate non-planar isomerizations of 5- and 6-vertex polyhedra by using their Gale diagrams which are 1- and 2-dimensional, respectively. Using this method, it is trivial to show that all degenerate non-planar isomerizations of 5-vertex polyhedra can be formulated as sequences of Berry pseudorotation processes, i.e. the prototypical diamond-square-diamond (dsd) process. The Gale diagrams of the 7 combinatorically distinct 6-vertex polyhedra consist necessarily of points on the circumference of the unit circle as well as the center in the case of the pentagonal pyramid. Study of allowed motions of these points along the circumference of the unit circle in these Gale diagrams reveal 6 different types of single or multiple parallel dsd processes or closely related dsd' or sds processes connecting these 7 combinatorically distinct 6-vertex polyhedra. In addition, a study of allowed motions of the points on the circumference of the Gale diagrams of the 6-vertex polyhedra through the center reveal 2 additional degenerate non-planar isomerization processes of 6-vertex polyhedra which involve pentagonal pyramid intermediates.

Key words: Topology—Gale diagrams—Polyhedral isomerizations—Diamond-square-diamond processes.

1. Introduction

Research during the past several years has led to a variety of approaches for the theoretical treatment of stereochemical non-rigidity in ML$_n$ coordination complexes (M = central atom, generally a metal; L = ligands surrounding M). Thus,
possible isomerizations of ML_n polyhedra [n = 4 Ref. [2], 5 Ref. [3], 6 Ref. [4], and 8 Ref. [5]] have been represented topologically [2, 6] as graphs in which the vertices represent different polyhedral isomers and the edges represent possible one-step isomerizations. The individual polyhedral isomerizations have been described in terms of so-called diamond-square-diamond (dsd) processes [7]. In these terms the inherent fluxionality of polyhedra can be related to topological features which correspond to the ability of an individual polyhedron to isomerize to an equivalent polyhedron through a dsd process [8].

A question which is not clear from these and related theoretical studies is the extent to which all possible polyhedral isomerizations can be represented as dsd processes. The general impression from all of the theoretical work on polyhedral rearrangements is that specific polyhedra and specific polyhedral isomerization processes are selected without any attempt to determine all possible polyhedra and polyhedral isomerizations for a given coordination number. Actually from the chemical point of view, the first (and easier) half of this problem is essentially solved since all polyhedra having up to 8 vertices have been characterized [9] albeit as their duals [10] (i.e. polyhedra having no more than 8 faces). This paper presents a solution of the second half of the problem for polyhedra with 5 and 6 vertices by using Gale diagrams [10] to study all possible vertex motions in these polyhedra.

2. Background

Consider the polyhedron formed by the ligand donor atoms L in an ML_n coordination complex or the vertex atoms in a metal cluster, polyhedral borane, etc. Properties of such polyhedra which have been characterized in previous papers include their topologies [11] (vertex, edge, and face relationships) and symmetries (automorphism (point) groups [12] or chirality functions [13]). Polyhedra may also be characterized by their vertex plane structure. A vertex plane of a polyhedron is any plane containing 3 or more vertices of the polyhedron. All faces of the polyhedron are necessarily vertex planes. In addition, all polyhedra except the tetrahedron also have non-facial vertex planes, i.e. vertex planes which are not faces. The simplest example of a non-facial vertex plane is the plane formed by the 3 equatorial vertices of a trigonal bipyramid.

A minimum of 3 points is needed to define a plane. Therefore, a vertex plane containing only 3 vertices is an ordinary vertex plane. Special vertex planes, on the other hand, contain 4 or more vertices. Since a polyhedron with v vertices is by definition a 3-dimensional figure, no vertex planes in any polyhedron can contain all v vertices. A polyhedron with a necessarily facial vertex plane containing v-1 vertices is a pyramid. A polyhedron with a non-facial vertex plane containing v-2 vertices is a bipyramid.

A polyhedral isomerization step may be defined [6] as a deformation of a specific polyhedron P_1 to the point that the vertices define a new polyhedron P_2. Of particular interest in the context of this work are sequences of two polyhedral