

Chemical applications of topology and group theory. 26*. The sextuple diamond–square–diamond rearrangement of the icosahedron through a cuboctahedron intermediate[☆]

R. Bruce King

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

The details of the symmetry factoring of the graphs corresponding to the icosahedron and the cuboctahedron are presented. Such symmetry factoring procedures use the sequence of twofold C_2 and threefold C_3 elements $C_2 \times C_2 \times C_2 \times C_3$ to give disconnected graphs having eigenvalue spectra similar to those of the original polyhedra but with components having only one and two vertices. In addition, the same symmetry factoring sequence is used to determine the eigenvalue spectrum of an intermediate in the sextuple diamond–square process for conversion of the icosahedron to the cuboctahedron.

1. Introduction

Two highly symmetrical 12-vertex polyhedra are the icosahedron (fig. 1) and cuboctahedron (fig. 2) which are of chemical significance in the following areas:

- (1) They are involved in rearrangements of 12-vertex boranes and carboranes such as $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$, as originally recognized by Lipscomb [2] and studied recently in much greater detail by Gimarc [3].
- (2) Boron icosahedra are basic building blocks in elemental boron and metal borides with high boron content [4,5].
- (3) Models for icosahedral quasicrystals [6–9] may be based on aluminum icosahedra.
- (4) These 12-vertex polyhedra occur in both centered metal carbonyl clusters such as the rhodium carbonyl hydrides $[Rh_{13}(CO)_{24}H_{5-q}]^{q-}$ ($q = 2-4$) [10, 11], in which the outer Rh_{12} cuboctahedron may be regarded as a 12-vertex “pseudodeltahedron”, and uncentered metal carbonyl clusters such as $[Ni_9(AsPh)_3(CO)_{15}]^{2-}$ and $[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$ containing Ni_9As_3 and $Ni_{10}As_2$ icosahedra, respectively [12].

*This paper is dedicated to Professor Frank Harary in recognition of his pioneering work in areas of graph theory closely related to chemical problems.

[☆]For part 25 of this series, see ref. [1].

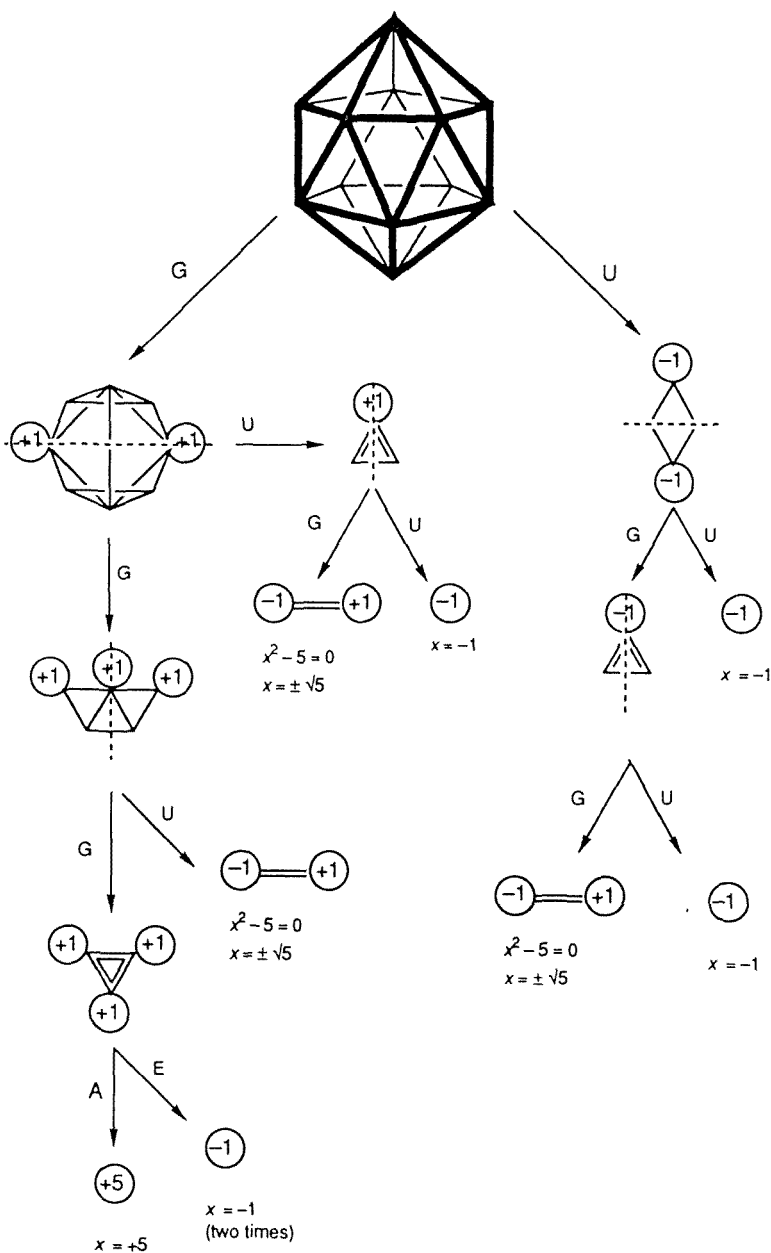


Fig. 1. The icosahedron and a schematic summary of its symmetry factoring using the sequence $C_2 \times C_2 \times C_2 \times C_3$. In the final stage, edges of weight 2 are written as double lines.

- (5) These 12-vertex polyhedra are found in polyoxometallates [13] such as the so-called Keggin ions $\text{XM}_{12}\text{O}_{40}^{n-}$ ($n = 3-7$); $M = \text{Mo}, \text{W}$; $X = \text{B}, \text{Si}, \text{Ge}, \text{P}, \text{Fe}^{\text{III}}, \text{Co}^{\text{II}}, \text{Cu}^{\text{II}}$, etc.) containing an M_{12} cuboctahedron and the Silverton ions $M^{\text{IV}}\text{Mo}_{12}\text{O}_{42}^{8-}$ ($M = \text{Ce}, \text{Th}$), in which the central metal M^{IV} forms an M_{12} icosahedron with the interior oxygen atoms.

Conversion of an icosahedron to a cuboctahedron can be visualized as a sextuple diamond-square process. Such a process is the first stage of a sextuple diamond-square-diamond rearrangement of an icosahedron through a cuboctahedron intermediate, which was first recognized by Lipscomb [2] already in 1966 and subsequently studied in greater detail by Gimarc and collaborators [3]. This paper compared in detail the spectra of the icosahedral and cuboctahedral graphs; such spectra are related to the bonding orbitals of these polyhedra in chemical structures.

The problem of determining the spectra of the icosahedron and cuboctahedron is an excellent illustration of symmetry factoring methods [14–21]. During the course of each symmetry factoring, a connected graph G with v vertices depicting the polyhedron in question is transformed into a disconnected graph G^* , also with v vertices but with c components G_1, \dots, G_c such that the eigenvalue spectrum of G^* is the same as that of G . However, whereas the determination of the spectrum of G requires the evaluation of a determinant of a $v \times v$ matrix followed by the solution of an equation of degree v , determination of the equivalent spectrum of G^* requires the evaluation of determinants of smaller matrices no larger than $u \times u$ followed by the solution of equations of lower degrees no higher than u , where $u < v$ is the number of vertices in the largest components of G^* . An important purpose of symmetry factoring is thus the reduction of the degrees of the algebraic equations which must be solved in order to determine the spectrum. In addition, the size of the matrix for which the determinant must be calculated is $u < v$. The high symmetries of the icosahedron and the cuboctahedron make it possible for the symmetry factoring procedure discussed in this paper to reduce the corresponding connected 12-vertex polyhedral graphs into disconnected graphs having only one- and two-vertex components.

2. Symmetry factoring studies

The topology of chemical bonding can be represented by a graph G in which the vertices correspond to atoms or orbitals participating in the bonding and the edges correspond to bonding relationships. Previous papers [22–25] have shown that the energy parameter E_k for molecular orbital k is related to the eigenvalues x_k of the adjacency matrix A as follows:

$$E_k = \frac{\alpha + x_k \beta}{1 + x_k S}. \quad (1)$$

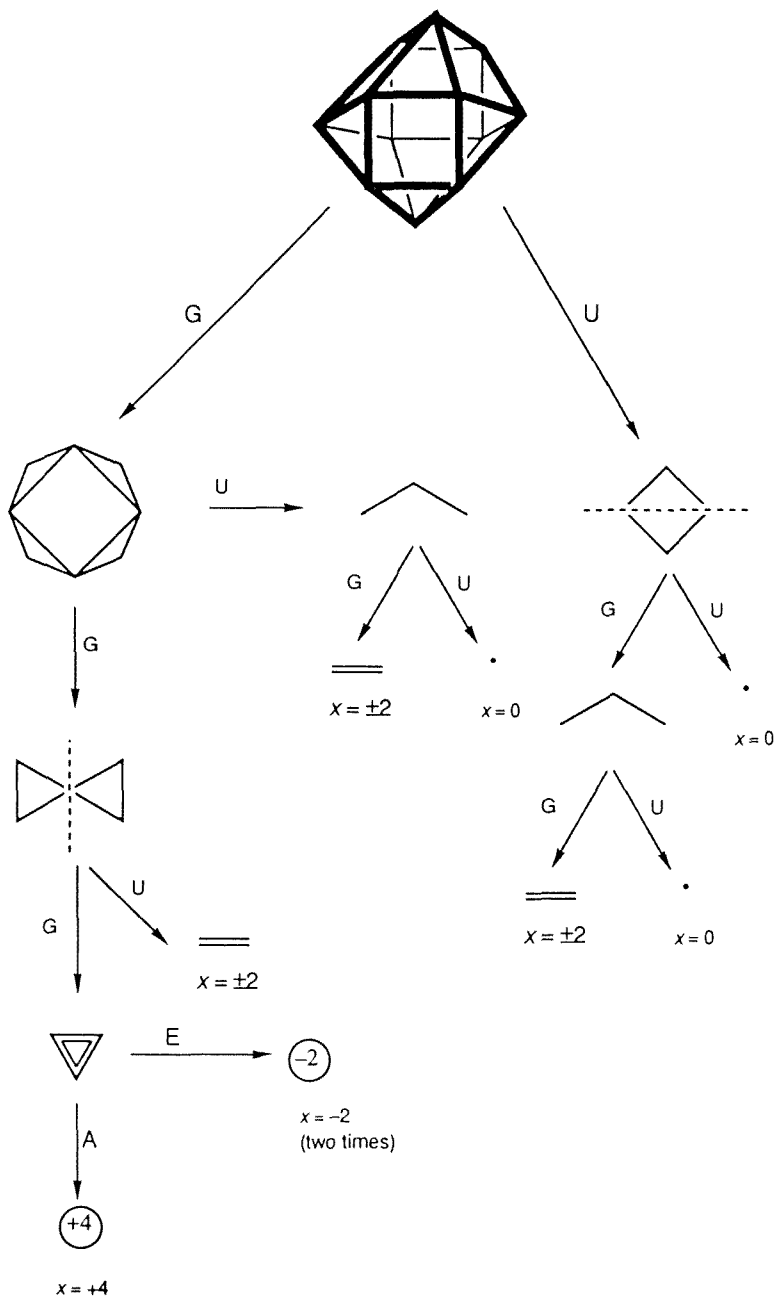


Fig. 2. The cuboctahedron and a schematic summary of its symmetry factoring using the sequence $C_2 \times C_2 \times C_2 \times C_3$.

The parameters α , β , and S of eq. (1) are the standard parameters of Hückel theory, namely the Coulomb integral, the resonance integral, and the overlap integral, respectively.

In order to determine the eigenvalues x_k of the adjacency matrices of the icosahedron (fig. 1) and cuboctahedron (fig. 2), symmetry factoring methods [17] are used as illustrated in figs. 1 and 2 for the icosahedron and cuboctahedron, respectively. In the symmetry factoring of the icosahedron, the fivefold axes are not used. Furthermore, in applying the simplest reported symmetry factoring procedure [17], threefold axes must be treated with caution since Rule E4 of ref. [17] is questionable. However, edges of the type E4 (ref. [17]) do not appear in the symmetry factoring of the icosahedron and cuboctahedron, so this is not a problem with the systems considered in this paper.

The symmetry factoring schemes outlined in figs. 1 and 2 for the icosahedron and cuboctahedron, respectively, use the tetrahedral subgroup contained in the point groups of each of these polyhedra. In order to avoid the difficulty with the threefold axes in the reported [17] procedure, the twofold axes are used first so that the symmetry factoring procedure used in both cases can be summarized as $C_2 \times C_2 \times C_2 \times C_3$. Each stage of symmetry factoring using a twofold axis leads to a so-called G branch (G = gerade) and a so-called U branch (U = ungerade) as indicated in figs. 1 and 2, where the gerade branches are the left branches and the ungerade branches are the right branches. The roots of the equations corresponding to each of these branches each lead to a single eigenvalue in the graph spectrum. Each stage of symmetry factoring using a threefold axis also leads to two branches, the A and E branches. The roots of the equations corresponding to the A branch appear once, but those corresponding to the E branch appear twice in the graph spectrum. In the cases of both the icosahedron (fig. 1) and the cuboctahedron (fig. 2) several symmetry factoring routes may lead to the same eigenvalues, thus providing eigenvalues of higher multiplicities, such as 3 and 5. Thus, in the case of the icosahedron the quintuply degenerate -1 eigenvalue arises twice from the GGGE symmetry factoring sequence and once each from the GUU, UU, and UGU symmetry factoring sequences (fig. 1), thus accounting for its observed multiplicity of five.

Figures 1 and 2 show that both the icosahedron and cuboctahedron have four distinct eigenvalues with patterns of multiplicities of 1, 3, 5, 3 and 1, 3, 3, 5 from the most positive eigenvalue down for the icosahedron and cuboctahedron, respectively. The multiplicity pattern of 1, 3, 5, 3 for the icosahedron corresponds to one anodal s orbital, three uninodal p orbitals, five binodal d orbitals, and three of the seven trinodal f orbitals, respectively, with the eigenvalues decreasing with increasing nodality, as expected. However, the multiplicity 5 eigenvalue of the cuboctahedron is unusual since its point group O_h has no irreducible representations of dimension higher than three. The possibility of this eigenvalue of multiplicity five of the cuboctahedron arising from the accidental coincidence of a doubly degenerate and a triply degenerate eigenvalue was investigated by a more detailed study of the symmetry factoring procedure.

The eigenvalues of both the icosahedron and cuboctahedron can be classified by their origins from the symmetry factoring procedure using G and U to designate the symmetric and antisymmetric branches arising from a twofold symmetry element, and A and E to designate the symmetric and antisymmetric branches from a threefold symmetry element, respectively (table 1). The -1 eigenvalue of multiplicity five

Table 1
Relationship between the eigenvalues of the icosahedron and those of the cuboctahedron.

Symmetry factoring branch	Number of eigenvalues	Icosahedron eigenvalue	Cuboctahedron eigenvalue
G^3A	1	5	4
G^3E	2	-1	-2
G^2U	6	$\pm\sqrt{5}$	± 2
GU^2	3	-1	0

of the icosahedron is seen to arise from the coincidence of a twofold degenerate G^3E branch with a threefold degenerate GU^2 branch. This coincidence is a consequence of the fivefold symmetry element not used in the symmetry factoring procedure. The -2 eigenvalue of the cuboctahedron of multiplicity five is seen to arise from the accidental coincidence of the threefold degenerate G^2U branch and the twofold degenerate G^3E branch. Thus, the eigenvalues of the icosahedron and the cuboctahedron of multiplicities five are seen to have different origins.

The identical symmetry factoring procedure using a $C_2 \times C_2 \times C_2 \times C_3$ sequence can also be applied to an intermediate stage in the sextuple diamond-square conversion of an icosahedron to a cuboctahedron in which the weight of one diagonal of each of the six square faces of a cuboctahedron (designated as a) is made 0.5 rather than 0 for an ideal cuboctahedron. In this case, a 1, 3, 3, 2, 3 multiplicity pattern without any accidental coincidences is obtained. The relationship between the eigenvalues of the icosahedron, the cuboctahedron with $a = 0.5$, and the ideal cuboctahedron with $a = 0$ is depicted in fig. 3.

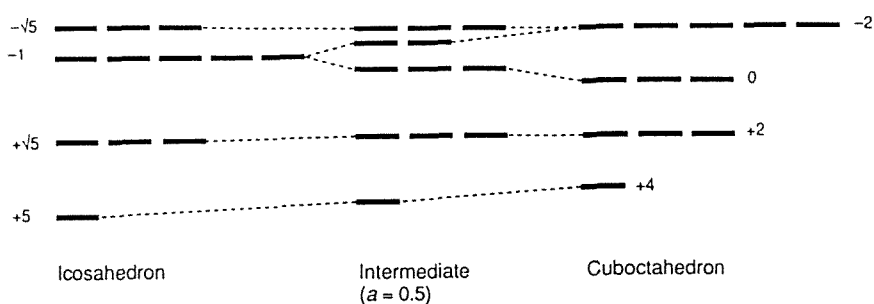


Fig. 3. The eigenvalue spectra of the icosahedron, cuboctahedron, and an intermediate ($a = 0.5$, see text) in the sextuple diamond-square process converting the icosahedron to a cuboctahedron.

3. Chemical implications

The eigenvalue spectra of the icosahedron and cuboctahedron can be related to the tensor surface harmonic theory as developed by Stone [26] and elaborated by Mingos and Johnston [27]. In a polyhedron with n vertices which is regarded as homeomorphic to the sphere, as in the case with deltahedra in globally delocalized cluster bonding [28–32], the single radial orbitals directed from each vertex towards the polyhedral center form a collection of n core molecular orbitals. These n core orbitals may be described by the scalar spherical harmonics, which correspond to the single S^σ , the three P^σ , the five D^σ , the seven F^σ orbitals, etc., of increasing energy and nodality. Figure 3 shows quite clearly that the distortion of the icosahedron to the cuboctahedron through a sextuple diamond–square process has a minor effect on the positive eigenvalues which represent the S^σ and P^σ bonding orbitals. The major reshuffling of the eigenvalues in going from the icosahedron to the cuboctahedron occurs with the negative eigenvalues which represent antibonding (virtual) orbitals of minor chemical significance.

A more specific chemical implication arises in the consideration of 12-vertex globally delocalized metal clusters containing interstitial atoms [10, 11]. Uncentered globally delocalized 12-vertex metal clusters such as $[\text{Ni}_9(\text{AsPh})_3(\text{CO})_{15}]^{2-}$ and $[\text{Ni}_{10}(\text{AsMe})_2(\text{CO})_{18}]^{2-}$ [12] as well as the deltahedral boranes $\text{B}_{12}\text{H}_{12}^{2-}$ and $\text{C}_2\text{B}_{10}\text{H}_{12}$ are icosahedra, whereas centered globally delocalized 12-vertex metal clusters $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_{5-q}]^{q-}$ ($q = 2-4$) may be cuboctahedra [10, 11] in order to have more space for the interstitial atom. The expansion of an icosahedron to a cuboctahedron, as might occur through a sextuple diamond–square process, is seen (fig. 3) to have relatively little effect on the energies of the skeletal bonding orbitals and therefore does not affect the stoichiometry leading to a closed shell electronic configuration.

References

- [1] R.B. King, *Inorg. Chem.* 30(1991)4437.
- [2] W.N. Lipscomb, *Science* 153(1966)373.
- [3] B.M. Gimarc, *J. Math. Chem.* 5(1990)359.
- [4] J.L. Hoard and R.E. Hughes, in: *The Chemistry of Boron and its Compounds*, ed. E.K. Muetterties (Wiley, New York, 1967) pp. 25–154.
- [5] D. Emin, T. Aselage, C.L. Beckel, I.A. Howard and C. Wood (eds.), *Boron-Rich Solids*, American Institute of Physics Conference Proceedings 140 (American Institute of Physics, New York, 1986).
- [6] D. Levine and P.J. Steinhardt, *Phys. Rev. Lett.* 53(1984)2477.
- [7] D. Levine and P.J. Steinhardt, *Phys. Rev.* B34(1986)596.
- [8] M. Audier, C. Janot, M. de Boissieu and B. Dubost, *Phil. Mag.* B60(1989)437.
- [9] R.B. King, *Inorg. Chim. Acta* 181(1991)217.
- [10] R.B. King, *Inorg. Chim. Acta* 116(1986)125.
- [11] R.B. King, *Int. J. Quant. Chem. Quant. Chem. Symp.* 20(1986)227.
- [12] D.F. Rieck, R.A. Montag, T.S. McKechnie and L.F. Dahl, *J. Am. Chem. Soc.* 108(1986)1330.
- [13] M.T. Pope, *Heteropoly and Isopoly Oxometallates* (Springer, Berlin, 1983).
- [14] B.J. McClelland, *J. Chem. Soc. Faraday Trans. II* 70(1974)1453.

- [15] B.J. McClelland, *Mol. Phys.* 45(1982)189.
- [16] B.J. McClelland, *J. Chem. Soc. Faraday Trans. II* 78(1982)911.
- [17] R.B. King, *Theor. Chim. Acta* 44(1977)223.
- [18] S.S. D'Amato, *Mol. Phys.* 37(1979)1363.
- [19] S.S. D'Amato, *Theor. Chim. Acta* 53(1979)319.
- [20] R.A. Davidson, *Theor. Chim. Acta* 58(1981)193.
- [21] M. Shen, *Int. J. Quant. Chem.* 38(1990)551.
- [22] K. Ruedenberg, *J. Chem. Phys.* 22(1954)1878.
- [23] H.H. Schmidtke, *J. Chem. Phys.* 45(1966)3920.
- [24] I. Gutman and N. Trinajstić, *Topics Curr. Chem.* 42(1973)49.
- [25] R.B. King, B. Dai and B.M. Gimarc, *Inorg. Chim. Acta* 167(1990)213.
- [26] A.J. Stone, *Polyhedron* 3(1984)1299.
- [27] D.M.P. Mingos and R.J. Johnston, *Struct. Bonding* 68(1987)29.
- [28] R.B. King and D.H. Rouvray, *J. Am. Chem. Soc.* 99(1977)7834.
- [29] R.B. King, in: *Chemical Applications of Topology and Graph Theory*, ed. R.B. King (Elsevier, Amsterdam, 1983) pp. 99–123.
- [30] R.B. King, in: *Molecular Structure and Energetics*, Vol. 1, ed. J.F. Liebman and A. Greenberg (VCH Publishers, Deerfield, 1986) pp. 123–148.
- [31] R.B. King, *J. Math. Chem.* 1(1987)249.
- [32] R.B. King, *Inorg. Chem.* 27(1988)1941.
- [33] R.B. King, *J. Math. Chem.* 4(1990)69.