

accepting N-heterocycles, a finding that provides some further aspects concerning the photochemically important control<sup>43</sup> of the relation between charge-transfer and ligand field excited states.

The lability of complexes **9** and **10** is also manifest in their redox chemistry. While the binuclear anion radicals **10**<sup>-</sup> show some persistence in solution, the oxidative process leading to Mn(II) is highly dissociative in the presence of coordinating DMF. Nevertheless, cyclic voltammetry of the Mn(I) complexes has allowed the construction of an electron-transfer/coordination scheme (Scheme II), which exhibits several interesting features such as ECE mechanisms for the oxidation of **10** and for the reduction of **9**.

Although dissociatively stable Mn(II)/Mn(I) mixed-valence dimers could not be obtained in the study presented, the recent characterization of the first such species at -40 °C<sup>44a</sup> and at ambient temperature<sup>44b</sup> suggests that the use of stronger, possibly negatively charged ligands may lead to more organometallic mixed-valence systems.

Summarizing, the present study focusing on pyrazine-bridged Mn(I) binuclear complexes reveals several aspects concerning the

possible electronic structures of such systems and demonstrates the use of the complementary physical techniques electron spectroscopy, electrochemistry, and electron spin resonance. In the absence of a detailed theoretical study of the system at hand<sup>45</sup> it should be pointed out that the results presented relate to recent calculations performed for the Creutz-Taube system **2**<sup>46</sup> and for binuclear dinitrogen complexes N<sub>2</sub>·2CpMn(CO)<sub>2</sub>,<sup>47</sup> both of which emphasize the crucial role of the interaction between the bridging ligand π\* level and the metal fragments for the bonding in such systems.

**Acknowledgment.** Work on electron-transfer reactivity of organometallics has been supported by Deutsche Forschungsgemeinschaft (DFG), Fonds der Chemischen Industrie, Flughafen Frankfurt/Main AG, and the Hermann Willkomm Foundation.

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(48) In this paper the periodic group notation is in accord with recent actions by the ACS nomenclature committee. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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## Chemical Applications of Topology and Group Theory. 20. Eight-Vertex Polyhedra and Their Rearrangements<sup>1</sup>

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There are 257 combinatorially distinct eight-vertex polyhedra, of which 14 are deltahedra. Of the 14 deltahedra, only the bisdisphenoid, commonly known as the *D*<sub>2d</sub> or triangular dodecahedron, both lacks tetrahedral chambers and can be formed by the hybridization of only s, p, and d orbitals. Degenerate single and symmetrical parallel multiple diamond-square-diamond processes involving the 14 eight-vertex deltahedra are tabulated. Among the eleven such processes (six single, two symmetrical double, one fully symmetrical triple, and two fully symmetrical quadruple), those relating the bisdisphenoid to the 4,4-bicapped trigonal prism and the square antiprism are of current chemical significance. Single, double, and quadruple dsd rearrangements of the bisdisphenoid are depicted as topologically equivalent cubes with added diagonals so that the pivot faces are faces of the underlying cube and the dsd processes involve shifting only the positions of selected diagonals without disturbing the 12 edges of the underlying cube.

### Introduction

Previous papers in this series have discussed new mathematical approaches for the treatment of stereochemical nonrigidity in ML<sub>n</sub> coordination complexes (M = central atom, generally a metal; L = ligands surrounding M) and metal clusters. Thus, Gale transformations<sup>2</sup> allow all possible nonplanar isomerization processes to be found for polyhedra having five and six vertices, i.e., corresponding to ML<sub>5</sub> and ML<sub>6</sub> complexes.<sup>3</sup> This Gale transformation approach is no longer effective for polyhedra having seven or more vertices, since Gale transforms no longer reduce the dimensionality of the problem.<sup>4</sup> However, the chemically based assumption<sup>4</sup> of minimum pivot face size in intermediate polyhedra coupled with the still manageable number of combinatorially distinct seven-vertex polyhedra, namely 34,<sup>5</sup> allows an

exhaustive study of chemically relevant diamond-square-diamond (dsd) processes<sup>6</sup> in seven-vertex polyhedra.<sup>4</sup>

This paper presents a related treatment of polyhedral isomerizations in eight-coordinate complexes. Here the problem is considerably more complicated since there are 257 combinatorially distinct eight-vertex polyhedra (Table I).<sup>5</sup> In order to make the problem tractable, the following two assumptions are used:

(1) Only dsd processes (i.e., 4-pyramidal rather than *n*-pyramidal (*n* ≥ 5) processes<sup>3</sup>) having a quadrilateral pivot face<sup>4</sup> will be considered. This assumption is justified on the energetic basis that polyhedra having one or more faces with five or more edges (i.e., pentagons, hexagons, heptagons, etc.) are unfavorable relative to polyhedra having only triangular and quadrilateral faces. This principle was already recognized in 1969 in the first paper of this series.<sup>7</sup>

(2) Only symmetrical parallel multiple dsd processes will be considered. In a symmetrical multiple dsd process the quadrilateral

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(2) Grünbaum, B. "Convex Polytopes"; Interscience: New York, 1967; Chapter 6.  
(3) King, R. B. *Theor. Chim. Acta* **1984**, *64*, 439.  
(4) King, R. B. *Inorg. Chem.* **1985**, *24*, 1716.  
(5) Federico, P. J. *Geometriae Dedicata* **1975**, *3*, 469.

- (6) Lipscomb, W. N. *Science* **1966**, *153*, 373.  
(7) King, R. B. *J. Am. Chem. Soc.* **1969**, *91*, 7211.

**Table I.** The 257 Combinatorially Distinct Eight-Vertex Polyhedra Divided into 18 Classes<sup>a</sup>

<i>v</i>	<i>e</i>	face types						no. of polyhedra	class
		<i>f</i>	<i>f</i> <sub>3</sub>	<i>f</i> <sub>4</sub>	<i>f</i> <sub>5</sub>	<i>f</i> <sub>4</sub> (=q)	<i>f</i> <sub>3</sub> (=t)		
8	18	12	0	0	0	0	12	14	A
8	17	11	0	0	0	1	10	38	B
8	16	10	0	0	1	0	9	12	C
8	16	10	0	0	0	2	8	64	D
8	15	9	0	1	0	0	8	3	E
8	15	9	0	0	1	1	7	24	F
8	15	9	0	0	0	3	6	47	G
8	14	8	1	0	0	0	7	1	H
8	14	8	0	1	0	1	6	2	I
8	14	8	0	0	1	2	5	20	J
8	14	8	0	0	2	0	6	2	K
8	14	8	0	0	0	4	4	17	L
8	13	7	0	1	0	2	4	2	M
8	13	7	0	0	1	3	3	5	N
8	13	7	0	0	2	1	4	2	O
8	13	7	0	0	0	5	2	2	P
8	12	6	0	0	0	6	0	1	Q
8	12	6	0	0	2	2	2	1	R

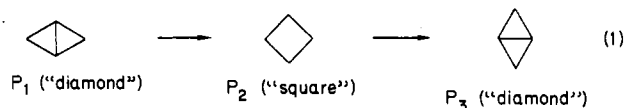
<sup>a</sup>*v* = number of vertices; *e* = number of edges; *f* = number of faces; *f*<sub>*n*</sub> = number of faces having *n* edges; *f*<sub>3</sub> = t (triangle) and *f*<sub>4</sub> = q (quadrilateral) for clarity.

pivot faces are equivalent because of the symmetry of the intermediate polyhedron.

In addition, the dsd processes in only the 14 combinatorially distinct eight-vertex deltahedra (Table II). are considered. In general, minimum-energy coordination polyhedra are deltahedra or polyhedra derived from deltahedra through low-energy processes. Furthermore, this paper shows that the two eight-vertex nondeltahedra of greatest significance as coordination polyhedra, namely the 4,4-bicapped trigonal prism and the square antiprism,<sup>8-11</sup> appear as intermediate polyhedra in single and double dsd processes of the bisdisphenoid ("D<sub>2d</sub>-dodecahedron"), the only one of the 14 eight-vertex deltahedra (Table II) found in ML<sub>8</sub> coordination complexes not involving f orbital elements.<sup>8-11</sup>

### Background

Many aspects of the methods used in this paper resemble those used in the previous paper on seven-coordinate complexes.<sup>4</sup> Thus, we consider sequences of polyhedral isomerizations P<sub>1</sub> → P<sub>2</sub> → P<sub>3</sub> in which polyhedra P<sub>1</sub> and P<sub>3</sub> are combinatorially equivalent; i.e., P<sub>1</sub> → P<sub>2</sub> → P<sub>3</sub> is a degenerate polyhedral isomerization. The intermediate polyhedron P<sub>2</sub> has fewer edges than P<sub>1</sub> (or P<sub>3</sub>). Since only dsd polyhedral isomerizations are considered, the polyhedral sequence P<sub>1</sub> → P<sub>2</sub> → P<sub>3</sub> has the following structure at the quadrilateral pivot face of P<sub>2</sub>:

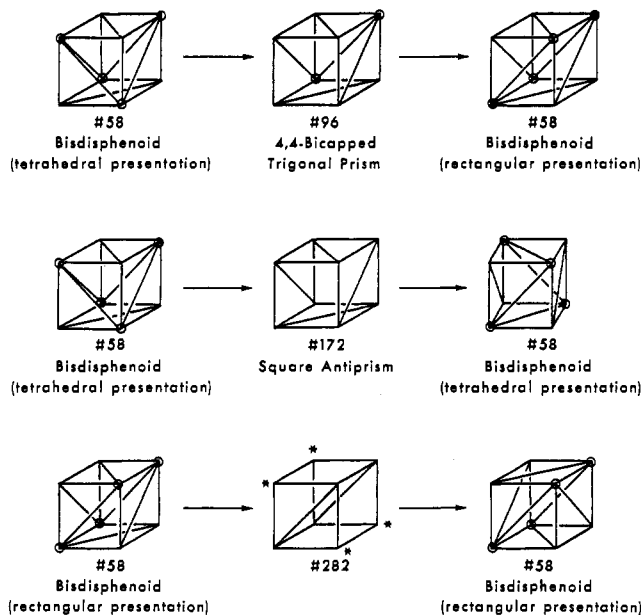


Thus, P<sub>1</sub> and P<sub>3</sub> can be generated from P<sub>2</sub> by drawing diagonals in two different ways across the quadrilateral pivot face of P<sub>2</sub>. In the case of symmetrical multiple dsd processes, the intermediate polyhedron P<sub>2</sub> has two or more quadrilateral pivot faces equivalent by symmetry and the multiple diagonals are drawn across these faces to preserve the symmetry elements making these faces equivalent.

With this method, the problem of finding all possible degenerate dsd polyhedral isomerizations of eight-vertex deltahedra can be reduced to the following:

(1) Find all eight-vertex polyhedra having only triangular faces except for a single quadrilateral face or several symmetrically equivalent quadrilateral faces. These polyhedra correspond to

(8) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235.  
 (9) Muettterties, E. L.; Wright, C. M. *Q. Rev. Chem. Soc.* **1967**, *21*, 109.  
 (10) Lippard, S. J. *Prog. Inorg. Chem.* **1967**, *8*, 109.  
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**Figure 1.** Single (top), double (middle), and quadruple (bottom) dsd processes of the bisdisphenoid depicted as topologically equivalent cubes with added diagonals so that the pivot face(s) are faces of the underlying cube and the dsd processes involve shifting only the positions of selected diagonals without disturbing the 12 edges of the underlying cube. Degree-5 vertices are circled, and degree-3 vertices are starred.

the intermediate polyhedron P<sub>2</sub> of sequence 1.

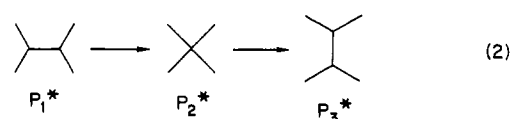
(2) Draw new polyhedra by adding diagonals in both ways across the quadrilateral pivot face of P<sub>2</sub> to generate the polyhedra P<sub>1</sub> and P<sub>3</sub>. If polyhedra P<sub>1</sub> and P<sub>3</sub> are combinatorially equivalent, then a degenerate eight-vertex deltahedral isomerization has been found. In the case of an intermediate polyhedron P<sub>2</sub> having two or more symmetrically equivalent quadrilateral faces, the diagonals to form P<sub>1</sub> and P<sub>3</sub> must be drawn so as to preserve the element of symmetry making equivalent the two or more quadrilateral faces of P<sub>2</sub>.

Federico<sup>5</sup> has tabulated all combinatorially distinct polyhedra having eight faces. These are the duals of the desired polyhedra having eight vertices where a dual P\* of P is obtained as follows:<sup>12</sup>

(1) The vertices of P\* are located at the midpoints of the faces of P.

(2) Two vertices of P\* are connected by an edge if and only if the corresponding faces of P share an edge.

The Schlegel diagrams<sup>13</sup> in Federico's paper are, of course, for the duals of the eight-vertex polyhedra of interest but can be used for this work if the dsd process of sequence 1 is expressed in dual form, i.e., sequence 2. In the dual transformation of sequence



1 into sequence 2, the quadrilateral pivot face of P<sub>2</sub> becomes a degree-four vertex in P<sub>2</sub>\* and the two new triangular faces in P<sub>1</sub> and P<sub>3</sub> generated by diagonals across this quadrilateral face become pairs of degree-3 vertices in P<sub>1</sub>\* and P<sub>3</sub>\*.

### Properties of the Eight-Vertex Polyhedra

Elementary topological considerations derivable from Euler's theorem<sup>7</sup> show that eight-vertex polyhedra must have at least six faces but no more than twelve faces. The 257 combinatorially distinct eight-vertex polyhedra can be divided into 18 classes (Table I) so that all members of a given class have the same set of polygon types for faces, i.e., the same face index.<sup>4</sup> Of these 18 classes, those classes having one or more faces with five or more edges

(12) Reference 2, pp 46-48.  
 (13) Reference 2, pp 42-46.

**Table II.** The 14 Combinatorially Distinct Eight-Vertex Deltahedra

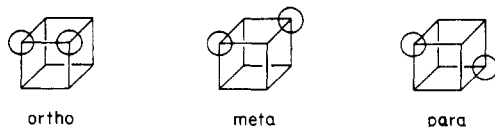
Federico no. of dual <sup>a</sup>	sym.	vertex types					sym dsd levels <sup>b</sup>	description <sup>b</sup>
		$v_7$	$v_6$	$v_5$	$v_4$	$v_3$		
(A) No Tetrahedral Chambers								
# 58	$D_{2d}$	0	0	4	4	0	1, 2, 4	bisdisphenoid (" $D_{2d}$ dodecahedron")
# 54	$D_{6h}$	0	2	0	6	0	0	hexagonal bipyramid
(B) Pentagonal-Bipyramidal Central Cavity: One Tetrahedral Chamber								
# 56	$C_3$	0	1	3	3	1	0	capped pentagonal bipyramid
(C) Octahedral Central Cavity: Two Tetrahedral Chambers								
# 57	$D_{3d}$	0	0	6	0	2	3	para-bicapped octahedron
# 55	$C_{2v}$	0	1	4	1	2	0	meta-bicapped octahedron
# 51	$C_{2v}$	0	2	2	2	2	1, 4	ortho-bicapped octahedron
# 53	$C_3$	0	2	1	4	1	1	capped capped octahedron (two levels of capping)
(D) No Cavity Larger Than a Tetrahedron (Bicapped Bicapped Tetrahedra): Five Tetrahedral Chambers								
# 45	$C_{2v}$	2	0	0	4	2	0	two 355 outer caps
# 46	$C_1$	1	1	2	1	3	1	445 + 355 outer caps
# 47	$C_1$	1	1	1	3	2	1	345 + 355 outer caps
# 48	$C_3$	1	0	3	2	2	0	two 345 outer caps
# 49	$T_d$	0	4	0	0	4	0	two 445 outer caps (symmetrically tetracapped tetrahedron)
# 50	$C_3$	0	3	1	1	3	0	345 + 445 outer caps
# 52	$C_2$	0	2	2	2	2	1, 2	two 345 outer caps

<sup>a</sup>See: Federico, P. J. *Geom. Ded.* **1975**, *3*, 469. <sup>b</sup>See text for a description of the nomenclature.

(i.e., the classes C, E, F, H, I, J, K, M, N, O, and R in Table I containing a total of 74 polyhedra) are unfavorable energetically and are therefore excluded from further consideration in this paper. The remaining seven classes (A, B, D, G, L, P, and Q in Figure 1) correspond to the 183 eight-vertex polyhedra containing only triangular and quadrilateral faces. These are the polyhedra potentially involved in the rearrangements discussed in this paper.

The eight-vertex deltahedra are of particular chemical interest. Table II lists the 14 combinatorially distinct eight-vertex deltahedra according to the size of the largest cavity or (equivalently in this case) the number of tetrahedral chambers. Note that there are only two eight-vertex deltahedra without tetrahedral chambers, the bisdisphenoid (" $D_{2d}$  dodecahedron") frequently occurring as an eight-vertex coordination polyhedron<sup>8-11</sup> and the hexagonal bipyramid, which is a "forbidden" eight-vertex polyhedron since the inversion center in its symmetry point group prevents it from being formed by the hybridization of only s, p, and d orbitals.<sup>14</sup> The special role of the bisdisphenoid in eight-coordinate metal complexes is already apparent.

The 12 remaining eight-vertex deltahedra, i.e., those having one or more tetrahedral chambers, follow the expected pattern. Since all ten (triangular) faces of the pentagonal bipyramid are equivalent, there is only one distinct capped pentagonal bipyramid (Federico number 56 of its dual). The four eight-vertex deltahedra having octahedral cavities can be best considered as their duals, namely cubes in which two vertices are truncated. The two vertices being truncated can be at each end of an edge (ortho, Federico number 51 of its dual), a face diagonal (meta, Federico number 55 of its dual), or a body diagonal (para, Federico number 57 of its dual).



The fourth eight-vertex deltahedron having an octahedral cavity (Federico number 53 of its dual) has two layers of capping. First, one of the eight equivalent faces of an octahedron is capped, giving three equivalent new triangular faces in place of the one face that was capped. A second cap is then placed on one of the three new triangular faces giving a "capped capped octahedron", i.e., a polyhedron with two levels of capping. Finally, Table II summarizes the properties of the seven combinatorially distinct

eight-vertex deltahedra formed by fusing five tetrahedra. One of these, the "tetracapped tetrahedron" (Federico number 49 of its dual), is distinctive in having relatively high  $T_d$  symmetry and only one level of capping relative to the central tetrahedron.

#### Rearrangements of Eight-Vertex Polyhedra

Table III summarizes all possible *symmetrical* dsd rearrangements of eight-vertex deltahedra in terms of the intermediate polyhedra ( $P_2$  in sequence 1) containing the quadrilateral pivot faces. Note that only a small number of these dsd rearrangements are degenerate, i.e., having combinatorially equivalent starting and finishing deltahedra. The possible number of symmetrical dsd rearrangements becomes smaller as a larger number of symmetrically equivalent quadrilateral pivot faces become involved in parallel processes.

Table III indicates six possible degenerate single dsd processes for eight-vertex deltahedra. By far the most interesting such process is the degenerate dsd rearrangement of the chemically significant bisdisphenoid (Federico number 58 of its dual) through a 4,4-bicapped trigonal-prism intermediate (Federico number 96 of its dual). The 4,4-bicapped trigonal-prism intermediate polyhedron occasionally appears in eight-coordinate structures (e.g., terbium (III) chloride).<sup>15</sup> The remaining five degenerate dsd processes involve eight-vertex deltahedra of low symmetry ( $C_1$ ,  $C_2$ , and  $C_3$ ) consisting of either five fused tetrahedra (Federico numbers 46, 47, and 52 of their duals) or the bilevel capped capped octahedron (Federico number 53 of its dual). These processes do not appear to be particularly significant chemically in eight-coordinate derivatives because of the unlikely polyhedra involved.

Table III indicates two possible degenerate symmetrical double dsd rearrangements of eight-vertex deltahedra. The chemically interesting process involves the degenerate double dsd rearrangement of the bisdisphenoid through a square-antiprism intermediate. The square antiprism is the eight-vertex nondeltahedron most frequently found in coordination compounds.<sup>8-11</sup> Also, the bisdisphenoid-square antiprism-bisdisphenoid double dsd rearrangement is included in a topological representation of hyperoctahedrally restricted eight-coordinated polyhedral rearrangements discussed several years ago.<sup>16</sup>

Symmetrical triple dsd rearrangements are necessarily rare since a  $C_3$  axis must be preserved throughout such processes. The single examples of such a degenerate eight-vertex process (Table III) involves rearrangement of a bicapped octahedron (Federico

(14) King, R. B. *Theor. Chim. Acta* **1984**, *64*, 453.

(15) Forrester, J. D.; Zalkin, A.; Templeton, D. H.; Wallmann, J. C. *Inorg. Chem.* **1964**, *3*, 185.

(16) King, R. B. *Theor. Chim. Acta* **1981**, *59*, 25.

Table III. Symmetrical DSD Processes of Eight-Vertex Deltahedra

intermediate polyhedron <sup>a</sup>	deltahedra formed by diagonalization <sup>a</sup>	remarks	intermediate polyhedron <sup>a</sup>	deltahedra formed by diagonalization <sup>a</sup>	remarks
(A) Single dsd Processes					
# 59 (11033- $C_1$ )	# 45 (20042- $C_{2v}$ ) and # 46 (11213- $C_1$ )		# 78 (01313- $C_1$ )	# 50 (03113- $C_s$ ) and # 55 (01412- $C_{2v}$ )	
# 60 (11033- $C_1$ )	# 45 (20042- $C_{2v}$ ) and # 47 (11132- $C_1$ )		# 79 (01313- $C_2$ )	# 50 (03113- $C_s$ ) and # 52 (02222- $C_2$ )	
# 61 (10304- $C_s$ )	# 46 (11213- $C_1$ )	degenerate	# 80 (01232- $C_1$ )	# 47 (11132- $C_1$ ) and # 56 (01331- $C_{2v}$ )	
# 62 (10223- $C_1$ )	# 47 (11132- $C_1$ ) and # 48 (10322- $C_s$ )		# 81 (01232- $C_2$ )	# 48 (10322- $C_s$ ) and # 55 (01412- $C_{2v}$ )	
# 63 (10223- $C_1$ )	# 46 (11213- $C_1$ ) and # 47 (11132- $C_1$ )		# 82 (01232- $C_1$ )	# 48 (10322- $C_s$ ) and # 53 (02141- $C_s$ )	
# 64 (10223- $C_s$ )	# 46 (11213- $C_1$ )		# 83 (01232- $C_s$ )	# 53 (02141- $C_s$ )	degenerate
# 65 (10142- $C_1$ )	# 47 (11132- $C_1$ ) and # 48 (10322- $C_s$ )	degenerate	# 84 (01232- $C_1$ )	# 51 (02222- $C_{2v}$ ) and # 56 (01331- $C_s$ )	
# 66 (02204- $C_1$ )	# 46 (11213- $C_1$ ) and # 50 (03113- $C_s$ )		# 85 (01232- $C_s$ )	# 55 (01412- $C_{2v}$ ) and # 56 (01331- $C_s$ )	
# 67 (02204- $C_{2v}$ )	# 49 (04004- $T_d$ ) and # 51 (02222- $C_{2v}$ )		# 86 (01232- $C_s$ )	# 52 (02222- $C_2$ )	degenerate
# 68 (02123- $C_1$ )	# 46 (11213- $C_1$ ) and # 51 (02222- $C_{2v}$ )		# 87 (01232- $C_1$ )	# 52 (02222- $C_2$ ) and # 53 (02141- $C_s$ )	
# 69 (02123- $C_1$ )	# 46 (11213- $C_1$ ) and # 53 (02141- $C_s$ )		# 88 (01151- $C_s$ )	# 54 (02060- $D_{6h}$ ) and # 56 (01331- $C_s$ )	
# 70 (02123- $C_1$ )	# 47 (11132- $C_1$ ) and # 50 (03113- $C_s$ )		# 89 (01151- $C_1$ )	# 53 (02141- $C_s$ ) and # 56 (01331- $C_s$ )	
# 71 (02123- $C_s$ )	# 47 (11132- $C_1$ )	degenerate	# 90 (00422- $C_{2v}$ )	# 51 (02222- $C_{2v}$ ) and # 58 (00440- $D_{2d}$ )	
# 72 (02123- $C_1$ )	# 47 (11132- $C_1$ ) and # 52 (02222- $C_2$ )		# 91 (00422- $C_1$ )	# 55 (01412- $C_{2v}$ ) and # 56 (01331- $C_s$ )	
# 73 (02123- $C_s$ )	# 50 (03113- $C_s$ ) and # 53 (02141- $C_s$ )		# 92 (00422- $C_s$ )	# 56 (01331- $C_s$ ) and # 57 (00602- $D_{3d}$ )	
# 74 (02042- $C_{2v}$ )	# 45 (20042- $C_{2v}$ ) and # 54 (02060- $D_{6h}$ )		# 93 (00422- $C_2$ )	# 52 (02222- $C_2$ ) and # 57 (00602- $D_{3d}$ )	
# 75 (02042- $C_1$ )	# 47 (11132- $C_1$ ) and # 53 (02141- $C_s$ )		# 94 (00341- $C_s$ )	# 53 (02141- $C_s$ ) and # 58 (00440- $D_{2d}$ )	
# 76 (01313- $C_1$ )	# 46 (11213- $C_1$ ) and # 56 (01331- $C_s$ )		# 95 (00341- $C_s$ )	# 56 (01331- $C_s$ ) and # 58 (00440- $D_{2d}$ )	
# 77 (01313- $C_1$ )	# 48 (10322- $C_s$ ) and # 52 (02222- $C_2$ )		# 96 (00260- $C_{2v}$ )	# 58 (00440- $D_{2d}$ )	degenerate <sup>b</sup>
(B) Symmetrical Double dsd Processes					
# 99 (10124- $C_s$ )	# 45 (20042- $C_{2v}$ ) and # 48 (10322- $C_s$ )		# 159 (00242- $C_2$ )	# 51 (02222- $C_{2v}$ ) and # 58 (00440- $D_{2d}$ )	
# 103 (02024- $C_2$ )	# 45 (20042- $C_{2v}$ ) and # 51 (02222- $C_{2v}$ )		# 161 (00242- $C_2$ )	# 54 (02060- $D_{6h}$ ) and # 58 (00440- $D_{2d}$ )	
# 105 (02024- $C_2$ )	# 45 (20042- $C_{2v}$ ) and # 52 (02222- $C_2$ )		# 162 (00242- $C_s$ )	# 54 (02060- $D_{6h}$ ) and # 55 (01412- $C_{2v}$ )	
# 117 (01214- $C_s$ )	# 49 (04004- $T_d$ ) and # 56 (01331- $C_s$ )		# 163 (00242- $C_{2v}$ )	# 54 (02060- $D_{6h}$ ) and # 57 (00602- $D_{3d}$ )	
# 136 (01052- $C_{2v}$ )	# 54 (02060- $D_{6h}$ ) and # 55 (01412- $C_{2v}$ )		# 165 (00242- $C_s$ )	# 53 (02141- $C_s$ ) and # 55 (01412- $C_{2v}$ )	
# 137 (01052- $C_s$ )	# 51 (02222- $C_{2v}$ ) and # 54 (02060- $D_{6h}$ )	degenerate	# 167 (00242- $C_2$ )	# 52 (02222- $C_2$ ) and # 57 (00602- $D_{3d}$ )	
# 139 (00404- $C_{2v}$ )	# 52 (02222- $C_2$ )		# 168 (00242- $C_2$ )	# 57 (00602- $D_{3d}$ ) and # 58 (00440- $D_{2d}$ )	
# 140 (00404- $D_{2d}$ )	# 49 (04004- $T_d$ ) and # 58 (00440- $D_{2d}$ )		# 171 (00161- $C_s$ )	# 56 (01331- $C_s$ ) and # 58 (00440- $D_{2d}$ )	
# 151 (00323- $C_s$ )	# 50 (03113- $C_s$ ) and # 56 (01331- $C_s$ )		# 172 (00080- $D_{4d}$ )	# 58 (00440- $D_{2d}$ )	degenerate <sup>c</sup>
# 152 (00323- $C_s$ )	# 51 (02222- $C_{2v}$ ) and # 57 (00602- $D_{3d}$ )				
(C) Symmetrical Triple dsd Processes					
# 191 (01034- $C_{3v}$ )	# 49 (04004- $T_d$ ) and # 54 (02060- $D_{6h}$ )		# 245 (00062- $D_{3h}$ )	# 57 (00602- $D_{3d}$ )	degenerate
# 194 (00305- $C_{3v}$ )	# 49 (04004- $T_d$ ) and # 57 (00602- $D_{3d}$ )				
(D) Symmetrical Quadruple dsd Processes <sup>d</sup>					
# 282 (00044- $D_{2h}$ )	# 51 (02222- $C_{2v}$ ) or # 58 (00440- $D_{2d}$ )	degenerate (for # 51 or # 58)	# 288 (00044- $D_{2d}$ ) (gyrofastigium)	# 58 (00440- $D_{2d}$ ) or # 51 (02222- $C_{2v}$ )	degenerate (for # 51 or # 58)
# 287 (00044- $D_{2d}$ )	# 49 (04004- $T_d$ ) and # 58 (00440- $D_{2d}$ )				

<sup>a</sup>The numbers of the polyhedra correspond to the numbers of their dual polyhedra given in Table I of: Federico, P. J. *Geometriae Dedicata* **1975**, *3*, 469. The vertex index  $v_7v_6v_5v_4v_3$  and the symmetry point group are given in parentheses after the polyhedron dual number. <sup>b</sup>This corresponds to the bisdisphenoid-4,4-bicapped trigonal prism-bisdisphenoid single dsd degenerate rearrangement. <sup>c</sup>This corresponds to the bisdisphenoid-square antiprism-bisdisphenoid symmetrical double dsd degenerate rearrangement. <sup>d</sup>Symmetrical quadruple dsd processes are more complicated since there are different symmetry-preserving ways of drawing diagonals across the four quadrilateral faces of polyhedra # 282, # 287, and # 288.

number 57 of its dual) through a 3,3-bicapped trigonal-prism intermediate (Federico number 245 of its dual) in a process resembling a Bailar twist<sup>17</sup> but with the two capping vertices not directly participating in the rearrangement.

Symmetrical quadruple dsd processes are more complicated since there are different symmetry-preserving ways of drawing diagonals across the four quadrilateral faces of the three eight-vertex polyhedra having four quadrilateral and four triangular faces and  $D_{2d}$  or  $D_{2h}$  symmetry (Federico numbers 282, 287, and 288 of their duals). Two generic degenerate symmetrical quadruple dsd processes are listed in Table III. Again one of these processes involves the bisdisphenoid, this time undergoing a degenerate rearrangement through one of the two polyhedral intermediates having four triangular and four quadrilateral faces (Federico numbers 282 or 288 of their duals).

Figure 1 depicts topologically single (top), double (middle), and quadruple (bottom) dsd processes of the bisdisphenoid representing all of the relevant eight-vertex polyhedra as topologically equivalent cubes with added diagonals. There are two such presentations of the bisdisphenoid as a cube with an added diagonal in each of the six square faces: the tetrahedral presentation (e.g., Figure 1 top left, center left, and center right) in which the four degree-5 vertices of the bisdisphenoid (circled in Figure 1) form the vertices of a tetrahedron, and the rectangular presentation (e.g., Figure 1 top right, bottom left, and bottom right) in which the four degree-5 vertices of the bisdisphenoid are coplanar and form the vertices of a rectangle. Presentations of the bisdisphenoid are selected for a given dsd process so that the pivot face(s) correspond to faces on the underlying cube and the dsd process involves shifting only the positions of selected diagonals without disturbing the 12 edges of the underlying cube.

The top rearrangement in Figure 1 is a single dsd rearrangement of the bisdisphenoid (Federico number 58 of its dual) through a 4,4-bicapped trigonal-prism (Federico number 96 of its dual) intermediate using the front face of the underlying cube as the pivot face. This process interchanges the tetrahedral and rectangular presentations of the bisdisphenoid. The middle rearrangement in Figure 1 is a double dsd rearrangement of the bisdisphenoid through a square-antiprism (Federico number 172 of its dual) intermediate using the front and back faces of the underlying cube as the two pivot faces. This process involves the tetrahedral presentation of the bisdisphenoid. The bottom rearrangement in Figure 1 is a quadruple dsd rearrangement of the bisdisphenoid through a polyhedron (Federico number 282 of its dual) having four triangular faces, four quadrilateral faces, four vertices of degree 4, four vertices of degree 3, and  $D_{2h}$  symmetry using the left, top, right, and bottom faces of the underlying cube as the four pivot faces. This process involves the rectangular presentation of the bisdisphenoid. The other quadruple dsd rearrangement of the bisdisphenoid through the  $D_{2d}$  gyrobifastigium (Federico number 288 of its dual) listed in Table III cannot be depicted by using either the tetrahedral or rectangular presentations of the bisdisphenoid so that a face of the underlying cube is the pivot face and only diagonals are shifted.

The three types of dsd rearrangements of the bisdisphenoid depicted in Figure 1 represent all symmetrical possibilities involving the tetrahedral and rectangular presentations of the bisdisphenoid. The single dsd rearrangement through the 4,4-bicapped trigonal

prism (Figure 1 top) interchanges the two presentations. The double dsd rearrangement through the square antiprism (Figure 1 middle) requires the tetrahedral presentation, but the quadruple dsd rearrangement (Figure 1 bottom) requires the rectangular presentation for both the starting and finishing bisdisphenoids in order for the pivot face of the intermediate polyhedron to be a face of the underlying cube. Thus a factor affecting the relative ease of the various dsd rearrangements of the bisdisphenoid can be the degree of distortion of an actual bisdisphenoid to conform to the presentations (i.e., tetrahedral or rectangular) required for the pivot face of the dsd rearrangement to be a face of an underlying cube. In this connection, the double dsd process involving a square-antiprism intermediate (Figure 1 middle) should be the most favorable since less distortion of an actual bisdisphenoid is required to give the tetrahedral presentation than the rectangular presentation on a cube because in an actual bisdisphenoid the four degree-4 vertices and the four degree-5 vertices are located at the vertices of subtetrahedra.<sup>8</sup>

### Conclusions

This paper shows how treatment of polyhedral isomerizations in systems having increasing numbers of vertices requires increasingly restrictive assumptions in order to keep the number of possibilities tractable. Thus for five- and six-vertex polyhedra the dimensionality reduction afforded by Gale transformations<sup>3</sup> allows all nontrivial (i.e., nonplanar) rearrangements to be found without any restrictive assumptions. For seven-vertex polyhedra, the smallest number of vertices for which Gale transformation does not offer dimensionality reduction, the assumption of no pentagonal (or hexagonal) faces suggested by energetic considerations (thereby restricting polyhedral rearrangements to dsd processes) is sufficient to reduce the possibilities to a manageable number.<sup>4</sup> The eight-vertex polyhedra treated in this paper require symmetry considerations in addition to energetic considerations in order to select from the intractable number of possibilities those of greatest chemical interest. Extension of this work to polyhedra having nine or more vertices not only goes beyond the scope of Federico's tables of polyhedra<sup>5</sup> but also is unattractive because of the intractably large number of possibilities and decreasing relevance to real chemical systems.

The analysis in this paper also underscores the special role of the bisdisphenoid (popularly known as the " $D_{2d}$  dodecahedron") in eight-coordination structures. The bisdisphenoid is the only eight-vertex deltahedron that has no tetrahedral chambers and that can be formed from  $sp^3d^4$  hybrid orbitals. In addition, the bisdisphenoid is unique among eight-vertex deltahedra in undergoing single, symmetrical double, and symmetrical quadruple dsd processes, as depicted in Figure 1. Furthermore, the intermediate (nondeltahedral) polyhedra in the single and symmetrical double dsd processes of the bisdisphenoid, namely the 4,4-bicapped trigonal prism and square antiprism, respectively, also occur in eight-coordinate complexes.<sup>8-11</sup> For these reasons the bisdisphenoid has as fundamental a role in the chemistry of eight-coordinate complexes as the octahedron has in the chemistry of six-coordinate complexes. However, the bisdisphenoid is highly fluxional whereas the octahedron is relatively rigid.<sup>18</sup>

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