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Chemical applications of topology and group theory

16. Forbidden coordination polyhedra*

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This paper characterizes *forbidden polyhedra*, which are polyhedra with fewer than 9 vertices which cannot be formed using only the 9*s*, *p*, and *d* atomic orbitals. In this connection polyhedra are of particular interest if their symmetry groups are direct product groups of the type $R \times C_s'$ in which R is a group containing only proper rotations and C_s' is either C_s or C_i in which the non-identity element is an inversion center or a reflection plane which is called the *primary plane* of the group $R \times C_s'$. Using this terminology polyhedra of the following types are shown always to be forbidden polyhedra: (1) Polyhedra having 8 vertices, such direct product symmetry point groups, and either an inversion center or a *primary* plane fixing either 0 or 6 vertices; (2) Polyhedra having a 6-fold or higher C_n rotation axis. However, these conditions are not necessary for a polyhedron to be forbidden since in addition to one 7-vertex polyhedron and ten 8-vertex polyhedra satisfying one or both of the above conditions there are two forbidden C_{3v} 8-vertex polyhedra which satisfy neither of the above conditions.

Key words: Forbidden polyhedra—Direct product groups—Symmetry groups.

1. Introduction

Most elements above atomic number 10 have *s*, *p*, and *d* orbitals available to participate in chemical bonding through formation of appropriate hybrid orbitals. Since such elements have one *s* orbital, three *p* orbitals, and five *d* orbitals, use of *s*, *p*, and *d* orbitals for chemical bonding can lead to coordination polyhedra with up to 9 $(=1+3+5)$ vertices. However, there are some polyhedra with 8 or less vertices which because of symmetry restrictions cannot be formed by any

* For part 15 of this series see reference 1.

combination of *s*, *p*, and *d* orbitals: such polyhedra can be called *forbidden polyhedra*. The first paper of this series published in 1969 [2] describes some of these polyhedra as polyhedra of "zero flexibility". This paper systematizes forbidden polyhedra in terms of the structure of their symmetry groups considered as permutation groups on their vertices.

2. Background

Consider the two groups G with m operations $E, g_2, \ldots, g_m$ and H with n operations $E, h_2, \ldots, h_n$ in which the operations of G and H are independent except for the identity. The *direct product* $G \times H$ contains mn paired operations of the type $EE, g_2E, \ldots, g_mE, Eh_2, g_2h_2, \ldots, g_mh_2, Eh_3, \ldots, g_{m-1}h_n, g_mh_n$ where EE is the identity of $G \times H$ and where because of the independence of the operations of G and H the order of the paired operations in $G \times H$ is immaterial [3].

The direct product $G \times H$ has the following properties:
(1) If G has the r conjugacy classes $K_1 = E, K_2, \ldots, K_r$ and H has the s conjugacy classes $L_1 = E, L_2, \ldots, L_s$ then the direct product $G \times H$ has the rs conjugacy classes $K_1L_1 = E, K_2L_1, \ldots, K_rL_1, K_1L_2, K_2L_2, \ldots, K_rL_2, K_1L_3, \ldots, K_{r-1}L_s, K_rL_s$. The irreducible representations and their characters have a similar product structure.
(2) The groups G and H are both normal subgroups of their direct product $G \times H$ where a normal subgroup is a subgroup consisting only of entire conjugacy classes. The direct product may also be regarded as a special case of the semi-direct product [4] $G \wedge H$ in which only the first of the two groups (namely G) needs to be a *normal* subgroup of the product. The full definition of a semidirect product is considerably more complicated than that of a direct product. Furthermore, the conjugacy classes, irreducible representations, and characters of a semidirect product do not have a simple relationship to those of the factors in contrast to a direct product.

All non-trivial symmetry point groups [5] except for C_s and C_i contain one or more proper rotations C_n ($n \geq 2$) in addition to the identity. In addition the point groups other than C_n, D_n, T, O, and I contain one or more improper rotations S_n where S_1 is a symmetry plane σ and S_2 is an inversion center i. All point groups containing improper rotations S_n are semidirect products of the type $R \wedge C_s'$ where C_s' is either C_s (i.e. $E + \sigma$) or C_i (i.e. $E + i$) and R is a group consisting of only the identity and proper rotations. Note that R is a normal subgroup of the semidirect product $R \wedge C_s'$. For convenience the non-identity operation (namely σ or i) in the factor C_s' will be called a *primary involution* and designated as S' since this operation is particularly important in the context of this paper. Note that some point groups can have more than one primary involution. The point group C_{2v} is the most important point group of this type in the context of this paper.

Some point groups are *direct* products of the type $R \times C_s'$ in which both R and C_s' are normal subgroups. These are listed in Table 1. Because of the direct

Table 1. Direct product structure of finite symmetry point groups having reflection planes and/or inversion centers

$C_{2v} = C_2 \times C_s$
$C_{2nh} = C_{2n} \times C_i = C_{2n} \times C_s$
$C_{(2n+1)h} = C_{2n+1} \times C_s$
$D_{2nh} = D_{2n} \times C_i = D_{2n} \times C_s$
$D_{(2n+1)h} = D_{2n+1} \times C_s$
$D_{(2n+1)d} = D_{2n+1} \times C_i$
$S_{4n+2} = C_{2n+1} \times C_i$
$T_h = T \times C_i$
$O_h = O \times C_i$
$I_h = I \times C_i$

product structure the primary involution in such a group is in a class by itself. The character tables of these direct product point groups are $2r \times 2r$ matrices of the following type in which r is the number of classes in R and $\boldsymbol{X}$ is an $r \times r$ matrix corresponding to the character table of R:

$$\begin{pmatrix} \boldsymbol{X} & \boldsymbol{X} \\ \boldsymbol{X} & -\boldsymbol{X} \end{pmatrix} \tag{1}$$

In the character table (1) half of the characters for the primary involution are equal to the corresponding characters of the identity. The corresponding irreducible representations may be called the *even* or symmetrical irreducible representations since if the primary involution is an inversion, these irreducible representations are usually designated in character tables with a "g" for "gerade". The remaining half of the characters in (1) for the primary involution are the negative of the corresponding characters of the identity. The corresponding irreducible representations may be called the *odd* or antisymmetrical irreducible representations since if the primary involution is an inversion these irreducible representations are normally designated in character tables with a "u" for "ungerade". A conclusion from these observations is that a reducible representation with zero character for the primary involution must be the sum of an equal number of even and odd irreducible representations. More generally let d^+ and d^- be the sums of the dimensions of the even and odd irreducible representations, respectively, forming the reducible representation having a character $\chi(S')$ for the primary involution. Then

$$\chi(S') = d^+ - d^-. \tag{2}$$

Now consider the transformation properties of the 9s, p, and d orbitals in the C_s' groups C_i and C_s. These are summarized in Table 2. Note that in both of these cases 6 of the orbitals are even or symmetrical and the remaining 3 orbitals are odd or antisymmetrical.

Consider an 8-vertex polyhedron whose symmetry point group is a direct product $R \times C_s'$. The character of the primary involution of the reducible representation corresponding to the vertex permutations under the symmetry point group is equal to the number of vertices which are not permuted by the primary involution

Table 2. Transformations of s, p, and d orbitals in two element C_s' groups

C_s' Group	Even s, p, and d orbitals Number	Types	Odd s, p, and d orbitals Number	Types
$C_s(\sigma_{xy})$	6	$s, p_x, p_y, d_{x2-y2}, d_{xy}, d_{z2}$	3	p_z, d_{xz}, d_{yz}
C_i	6	$s, d_{x2-y2}, d_{z2}, d_{xy}, d_{xz}, d_{yz}$	3	p_x, p_y, p_z
$C_2[C_2(z)]$	5	$s, p_z, d_{x2-y2}, d_{z2}, d_{xy}$	4	$p_x, p_y\ d_{xz}, d_{yz}$

(i.e. the number of points which remain fixed when the primary involution is applied). If the primary involution is an inversion, its character is necessarily zero since *all* vertices of a polyhedron are permuted by an inversion (i.e. an inversion fixes no vertices of a polyhedron). Therefore, the reducible representation of an 8-vertex polyhedron with an inversion center contains equal numbers of even and odd irreducible representations. This corresponds to a hybridization using 4 symmetrical and 4 antisymmetrical atomic orbitals. Since only 3 of the 9*s*, *p*, and *d* orbitals are antisymmetrical (Table 2), an 8 vertex polyhedron with an inversion center cannot be formed using only *s*, *p*, and *d* orbitals.

Similar arguments can also be used for 8-vertex polyhedra having a direct product group $R \times C_s'$ in which the primary involution is a reflection plane (called a *primary plane*). Such polyhedra with *no* vertices on a primary plane cannot be formed using only *s*, *p*, and *d* orbitals. However, 8-vertex polyhedra are also possible with 2, 4, or 6 vertices on a primary plane. In this case, the sums of the dimensions of even and odd irreducible representations can be found by the following equations derivable trivially from Eq. 2:

$$d^+ = (v + \chi(S'))/2 \tag{3a}$$

$$d^- = (v - \chi(S'))/2. \tag{3b}$$

These equations indicate that 8 vertex polyhedra ($v = 8$) with 6 vertices on a primary plane have 7 even irreducible (one-dimensional) representations. Since the maximum number of even *s*, *p*, and *d* orbitals is 6 (see Table 2), such 8-vertex polyhedra are forbidden.

Polyhedra with 7 vertices cannot have an inversion center but can have a primary plane provided that this plane contains 1, 3, or 5 of the 7 vertices. Equations 3*a* and 3*b* for $v = 7$ show that all of these situations lead to numbers of even and odd irreducible representations which can be accommodated by the *s*, *p*, and *d* orbitals (i.e. a maximum of 6 even irreducible one-dimensional representations for $\chi(S') = 5$ and a maximum of 3 odd irreducible one-dimensional representations for $\chi(S') = 1$). Thus, no 7-vertex polyhedra are forbidden because of the wrong number of vertices being fixed by the primary plane in contrast to the situation with 8-vertex polyhedra discussed above.

Another feature leading to forbidden polyhedra is a rotation axis C_n where $n \geqslant 6$. For example, no *s*, *p*, or *d* orbitals transform according to the B_1 irreducible representation arising from 6 vertices in a non-trivial orbit of a C_6 rotation axis. Thus, the 7-vertex hexagonal pyramid is forbidden; this is the only forbidden 7-vertex polyhedron.

Formation of 9-vertex polyhedra using *s*, *p*, and *d* orbitals is more difficult. In this case, the symmetries of the irreducible representations corresponding to the vertices of the polyhedron must match perfectly the symmetries of the 9*s*, *p*, and *d* orbitals. Forbidden polyhedra are thus much more frequent in the case of 9-vertex polyhedra than in the cases of 7- and 8-vertex polyhedra. In any case, the 9-vertex polyhedra are much less interesting mathematically and chemically and therefore are not treated in this paper.

3. Results

Federico [6] has compiled a list of the combinatorially distinct polyhedra with up to 8 faces. Taking the duals [7] of the polyhedra with 7 and 8 faces in his compilation leads to the 34 possible polyhedra with 7 vertices and the 257 possible polyhedra with 8 vertices. This list was used to check the ideas in the previous section of this paper.

Table 3 summarizes the important properties of all of the 7 and 8 vertex polyhedra which cannot be formed from hybrids of *s*, *p*, and *d* orbitals (i.e. the forbidden polyhedra). Note that of the 34 polyhedra with 7 vertices only the hexagonal pyramid is forbidden. Among the 257 polyhedra with 8 vertices, 12 polyhedra are forbidden.

The following specific information is given in table 3:
(1) Names of the polyhedra having established names. In most cases, these are the polyhedra of greatest chemical interest.
(2) The identification number used for the dual of the polyhedron in Federico's paper [6]. Schlegel diagrams [8] are given for the duals [7] in Federico's paper.
(3) The symmetry point group of the polyhedron indicating direct product structure where it is found.
(4) The total numbers of vertices (v), edges (e), and faces (f).
(5) The numbers of vertices v_n having degree n.
(6) The numbers of faces f_n with n sides (i.e. f_3 is the number of triangular faces, f_4 is the number of quadrilateral faces, f_5 is the number of pentagonal faces, etc.).
(7) The irreducible representation required for the hybrid orbitals for which sufficient *s*, *p*, and *d* orbitals are not available.
For example, in the case of the D_{3d} bicapped octahedron two A_{2u} orbitals are required but the only *s*, *p*, and *d* orbital of this type is the p_z orbital.

The forbidden polyhedra in Table 3 can be classified into the following categories:
(A) 8-vertex polyhedra having an inversion center: Federico numbers 54 (hexagonal bipyramid), 57 (bicapped octahedron), 282, 300 (cube), and 163.
(B1) 8-vertex polyhedra having a primary plane fixing no vertices: Federico numbers 245 (3,3-bicapped trigonal prism) and 291.

Table 3. Forbidden polyhedra with seven and eight vertices

Name (if any)	Federico number of dual	Symmetry point group	v	e	f	Vertex types v_3	v_4	v_5	v_6	Face types f_3	f_4	f_5	f_6	Forbidden irreducible representation
Hexagonal pyramid	19	C_{6v}	7	12	7	6	0	0	1	6	0	0	1	B_1
Hexagonal bipyramid	54	$D_{6h}=D_6\times C_i$	8	18	12	0	6	0	2	12	0	0	0	B_{1u}
Bicapped octahedron	57	$D_{3d}=D_3\times C_i$	8	18	12	2	0	6	0	12	0	0	0	$2A_{2u}$
3,3-Bicapped triagonal prism	245	$D_{3h}=D_3\times C_s$	8	15	9	2	6	0	0	6	3	0	0	$2A_2''$
	282	$D_{2h}=D_2\times C_i$	8	14	8	4	4	0	0	4	4	0	0	$2B_{3u}$
Cube	300	$O_h=O\times C_i$	8	12	6	8	0	0	0	0	6	0	0	A_{2u}
Dual of triangular cupola	191	C_{3v}	8	15	9	4	3	0	1	6	3	0	0	$4A_1$
	194	C_{3v}	8	15	9	5	0	3	0	6	3	0	0	$4A_1$
	45	$C_{2v}=C_2\times C_s$	8	18	12	2	4	0	$2v_7$	12	0	0	0	$3B_2$
	74	$C_{2v}=C_2\times C_s$	8	17	11	2	4	0	2	10	1	0	0	$3B_1$
	291	$C_{2v}=C_2\times C_s$	8	13	7	6	2	0	0	4	2	0	1	$3B_1$
	163	$C_{2h}=C_2\times C_i$	8	16	10	2	4	2	0	8	2	0	0	$3B_u$
Heptagonal pyramid	247	C_{7v}	8	14	8	7	0	0	$1v_7$	7	0	0	1_{f7}	$3B_u$

(B2) 8-vertex polyhedra having a primary plane fixing 6 vertices: Federico numbers 45 and 74.
(C) Polyhedra having a 6-fold or higher C_n rotation axis: Federico numbers 19 (hexagonal bipyramid) and 247 (heptagonal pyramid).
(D) Other forbidden polyhedra: Federico numbers 191 and 194 corresponding to 2 rather unusual C_{3v} 8-vertex polyhedra.

Some of these polyhedra belong to more than one of the above categories, e.g. the cube belongs to categories *A* and *B*1 and the hexagonal bipyramid belongs to categories *A* and *C*. The existence of polyhedra of category *D* means that the presence of an inversion center, a primary plane containing 0 or 6 vertices, and/or 6-fold or higher rotation axis are sufficient but not necessary conditions for an 8-vertex polyhedron to be forbidden.

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