Inorg. Chem. 1981, 20, 363-372

Hamilton and Ibers[70] suggested as a criterion for existence of a hydrogen bond, it excludes the resulting C–H···O, N–H···O, and O–H···O angles of less than 126°, a value which is considered to be unrealistically small. It can be seen in Figure 4 that oxygens of the non-metal-bonding nitrate ion [containing N(33)] act as acceptor sites through H(1) and H(6a) of the adeninium moiety and the H(a) atom of the water molecule. The existence of this weakly binding nitrate ion in the molecule may explain in part the rather unstable nature of the crystal to X irradiation. It is noted that the imidazole carbon atom C(8) is also involved in a short contact with one of the nitrate oxygen atoms. This type of weak interaction involving the C(8)–H group has previously been observed in a number of structures (see ref 43c, and references cited therein, and ref 55).

Shown in Figure 5 is a stereoscopic view of the unit-cell packing.

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Registry No. $[(C_5H_6N_5)Cd(NO_3)_2 \cdot H_2O]_2(NO_3)_2$, 75626-83-4; adenosine-5′-monophosphoric acid monosodium salt, 132-00-3.

Supplementary Material Available: A table of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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Chemical Applications of Topology and Group Theory. 9. The Symmetries of Coordination Polyhedra[1]

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The point groups of three-dimensional polyhedra with n vertices including those of importance as coordination polyhedra in ML_n complexes are considered as subgroups of the fully symmetric permutation group P_n with $n!$ elements. The terms in the cycle index of P_n are first classified into those forbidden and those allowed for three-dimensional symmetry operations. Subsets of the allowed cycle index terms of P_n can then be chosen in different ways to correspond to the permutations representing symmetry operations in different families of polyhedra with n vertices. Thus the point groups D_{3h}, C_{4v}, and D_5 for the five-vertex figures trigonal bipyramid, square pyramid, and planar pentagon, respectively, can be obtained from the fully symmetric group P_5 by deletion of the (4 + 5)-fold, the (3 + 5)-fold, and the (3 + 4)-fold rotation terms, respectively. For coordination numbers 6, 8, and 9, subgroups Q_n of the fully symmetric group P_n can be found which span all of the symmetries of the chemically feasible polyhedra for these coordination numbers. Thus for coordination number 6, the octahedral group O_h or $P_3[P_2]$ is an effective Q_6 since it spans the symmetries of all possible six-coordinate polyhedra except for the pentagonal pyramid, which is not feasible as a coordination polyhedron. Similarly, for coordination number 8, the wreath product group $P_4[P_2]$ with 384 elements corresponding to the symmetries of the four-dimensional analogue of the octahedron is an effective Q_8 since it spans the symmetries of all of the chemically reasonable eight-coordinate polyhedra including the cube, square antiprism, and hexagonal bipyramid. For coordination number 9, the pair group $P_2[P_3]^{(2)}$ with only 72 elements spans as well as the fully symmetric P_9 group with $9! = 362\,880$ elements the symmetries of the chemically feasible nine-coordinate polyhedra.

Introduction

In 1969 I published a topological method for generating possible polyhedra for coordination numbers 4–9, inclusive.[2] This approach considered maximum symmetry polyhedra with numbers of vertices (v), edges (e), and faces (f) satisfying the relationships $e + 2 = v + f$ (Euler's relationship), $2e \geq 3f$, $3v \leq 2e$, and $4 \leq v \leq 9$ and avoiding polyhedra containing one or more pentagonal or higher polygonal faces. Among such polyhedra those corresponding to the various possible sp^{3}d^n hybrids were next examined. Such polyhedra with minimum flexibilities (number of possible different sp^{3}d^n hybrids), maximum symmetries, and maximum numbers of faces were found to be favored in actual ML_n complexes.

This topological approach for generating polyhedra is attractive since a small number of rather elementary principles and assumptions provides a basis for extracting from the large numbers of possible polyhedra[3,4] those of chemical significance. Furthermore, combination of this topological approach[2] with rather elementary interligand electrostatic repulsion calculations in ML_n complexes[5–12] removes the need for some of the more difficultly justifiable assumptions of the topological treatment[2] including particularly the assumptions of flexibility minimization and avoidance of faces with five or more edges. Nevertheless, the topological approach of my earlier paper,[2] despite possible improvements, has the following inherent limitations for generating chemically significant coordination polyhedra. (1) In the cases of less symmetrical coordination complexes the question of which of several relatively unsymmetrical idealized coordination polyhedra most closely represents that found in an actual structure (such as that found by an X-ray diffraction study) may be ambiguous. (2) Ste-

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Table I. Cycle Indices Z (P_n) for the Symmetric Permutation Groups up to P_9

n	t	t^*	cycle index
2	2	2	$2Z(P_2) = x_1^2 + x_2$
3	3	3	$6Z(P_3) = x_1^3 + 3x_1x_2 + 2x_3$
4	5	5	$24Z(P_4) = x_1^4 + 6x_1^2x_2 + 8x_1x_3 + 3x_2^2 + 6x_4$
5	7	7	$120Z(P_5) = x_1^5 + 10x_1^3x_2 + 20x_1^2x_3 + 15x_1x_2^2 + 30x_1x_4 + 20x_2x_3 + 24x_5$
6	11	9	$720Z(P_6) = x_1^6 + 15x_1^4x_2 + 40x_1^3x_3 + 45x_1^2x_2^2 + 90x_1^2x_4 + 120x_1x_2x_3 + 144x_1x_5 + 15x_2^3 + 90x_2x_4 + 40x_3^2 + 120x_6$
7	15	9	$5040Z(P_7) = x_1^7 + 21x_1^5x_2 + 70x_1^4x_3 + 105x_1^3x_2^2 + 210x_1^3x_4 + 420x_1^2x_2x_3 + 504x_1^2x_5 + 105x_1x_2^3 + 630x_1x_2x_4 + 280x_1x_3^2 + 840x_1x_6 + 210x_2^2x_3 + 504x_2x_5 + 420x_3x_4 + 720x_7$
8	22	12	$40\,320Z(P_8) = x_1^8 + 28x_1^6x_2 + 112x_1^5x_3 + 210x_1^4x_2^2 + 420x_1^4x_4 + 1120x_1^3x_2x_3 + 1344x_1^3x_5 + 420x_1^2x_2^3 + 2520x_1^2x_2x_4 + 1120x_1^2x_3^2 + 3360x_1^2x_6 + 1680x_1x_2^2x_3 + 4032x_1x_2x_5 + 3360x_1x_3x_4 + 5760x_1x_7 + 105x_2^4 + 1260x_2^2x_4 + 1120x_2x_3^2 + 3360x_2x_6 + 2688x_3x_5 + 1260x_4^2 + 5040x_8$
9	30	12	$362\,880Z(P_9) = x_1^9 + 36x_1^7x_2 + 168x_1^6x_3 + 378x_1^5x_2^2 + 756x_1^5x_4 + 2520x_1^4x_2x_3 + 3024x_1^4x_5 + 1260x_1^3x_2^3 + 7560x_1^3x_2x_4 + 3360x_1^3x_3^2 + 7560x_1^2x_2^2x_3 + 945x_1x_2^4 + 10\,080x_1^3x_6 + 18\,144x_1^2x_2x_5 + 15\,120x_1^2x_3x_4 + 25\,920x_1^2x_7 + 11\,340x_1x_2^2x_4 + 10\,080x_1x_2x_3^2 + 30\,240x_1x_2x_6 + 24\,192x_1x_3x_5 + 11\,340x_1x_4^2 + 45\,360x_1x_8 + 2520x_2^3x_3 + 9072x_2^2x_5 + 15\,120x_2x_3x_4 + 25\,920x_2x_7 + 2240x_3^3 + 20\,160x_3x_6 + 18\,144x_4x_5 + 40\,320x_9$

reochemical nonrigidity[13-15] may obscure the real distinctions between some of the less symmetrical coordination polyhedra. Thus interchange of equivalent structures in stereochemically nonrigid systems involves breaking and making edges between various vertex pairs. The topology of stereochemically nonrigid systems thus is not invariant. The topological approach thus may overemphasize the importance of edges connecting pairs of L ligands in the coordination polyhedra of ML_n complexes where, in general, except for three-membered ring chelates (e.g., metallacyclopropanes), there are no direct chemical bonds between the donor atoms of ligand pairs.

This paper presents an alternative and complementary approach to the generation of coordination polyhedra. This approach considers in a well-defined manner the *symmetries* rather than the *topologies* of the coordination polyhedra. Thus a search for possible polyhedra for an n-coordinate complex ML_n starts with the symmetric group P_n of $n!$ permutations for the n ligands. Appropriate maximum symmetry subgroups of P_n are then selected which can be isomorphic with three-dimensional point groups[16] representing polyhedra with n vertices. These polyhedra are regarded as the *fundamental polyhedra* for coordination number n. They represent the most symmetrical possible polyhedra for n-coordinate complexes ML_n provided that they can be formed by hybrids of the available M orbitals (generally sp^3d^n). Less symmetrical polyhedra may be formed by distortions of the fundamental polyhedra and therefore have symmetry point groups which are subgroups of those of the corresponding fundamental polyhedra. A fundamental polyhedron with n vertices together with possible lower symmetry polyhedra formed by its distortion may be considered as a *family* of polyhedra for coordination number n. The treatment discussed in this paper thus seeks to classify the possible polyhedra for coordination numbers 4–9 into a limited number of polyhedron families. Those families where the fundamental polyhedron (or a distortion thereof retaining some characteristic symmetry) is realizable by a hybridization of the available M orbitals correspond remarkably closely to the polyhedra found in actual ML_n coordination complexes.

Permutation Groups and Cycle Indices

For an ML_n complex consider a 2 × n matrix

$$\mathrm{P}_n = \begin{pmatrix} 1 & 2 & 3 & \cdots & n \\ p_1 & p_2 & p_3 & \cdots & p_n \end{pmatrix}$$

where the top row represents vertex labels in the polyhedral skeleton and the bottom row represents ligand labels. The number $p_1, p_2, ..., p_n$ can be taken to run through the integers 1, 2, ..., n in some sequence. Such a matrix $\mathbf{P}_n$ can represent a given configuration or isomer of an ML_n complex; such configurations or isomers are frequently called *permutational isomers*.[17] For a given n there are $n!$ possible different $\mathbf{P}_n$ matrices. Now consider the matrix $\mathbf{P}^\circ_n$ where the bottom row $p_1, p_2, ..., p_n$ has the integers in the natural order 1, 2, 3, ..., n (i.e., the bottom row of $\mathbf{P}^\circ_n$ is identical with the top row). This matrix $\mathbf{P}^\circ_n$ can be taken to represent the *reference isomer*.

A group[16,18] can be defined relating the $\mathbf{P}_n$ matrices for a given n by considering *permutation isomerizations*.[19] First redefine the rows of $\mathbf{P}_n$ so that the top row represents the ligand labels of the reference isomer P°_n and the bottom row represents the ligand labels in any of the $n!$ possible permutations of its ligands. These permutations form a group of order $n!$ with the permutation leaving the reference isomer unchanged (i.e., that represented by $\mathbf{P}^\circ_n$ as so redefined) corresponding to the identity operation. This permutation group is called *the symmetric group of degree n* and is conventionally[18] represented as S_n. However, in this paper the symbol P_n rather than S_n will be used to represent the symmetric group of degree n in order to avoid confusion with the symbols used for improper rotations.[16]

Now consider the nature of the operations in a symmetric permutation group P_n. These operations are permutations of labels which can be written as a product of cycles which operate on mutually exclusive sets of labels, e.g., eq 1. The cycle

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 4 & 5 & 1 & 3 & 6 \end{pmatrix} = (1 \ \ 2 \ \ 4)(3 \ \ 5)(6) \tag{1}$$

structure of a given permutation in the group P_n can be represented by a sequence of indexed variables, i.e., $x_1x_2x_3$ for the permutation in eq 1. A characteristic feature of the *symmetric* permutation groups P_n for all n is that all permutations with the same cycle structure belong to the same conjugacy class.[20] Furthermore, no two permutations with different cycle structures can belong to the same conjugacy class. Therefore, for the symmetric permutation group P_n (but not necessarily for any of its subgroups) the cycle structures of permutations are sufficient to define their conjugacy classes. Furthermore, the number of conjugacy classes of the symmetric group P_n corresponds to the number of different partitions of n where a partition of n is defined as a set of positive integers $i_1, i_2, ..., i_k$ whose sum[20]

$$\sum_{j=1}^{k} i_j = n$$

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More detailed indications of the conjugacy classes of the symmetric groups P_n are given by their cycle indices.[21,22] A *cycle index* $Z(P_n)$ for a permutation group P_n is a polynomial of the form in eq 2, where c = number of classes (partitions

$$Z(P_n) = \sum_{i=1}^{i=c} a_i x_1^{c_{i1}} x_2^{c_{i2}} \ldots x_n^{c_{in}} \tag{2}$$

of n), a_i = number of elements of P_n in class i, x_j = dummy variable referring to cycles of length j, and c_{ij} = exponent indicating the number of cycles of length j in class i. These parameters in the cycle indices of the symmetric groups P_n must satisfy the following relationships. (1) Each of the $n!$ permutations of P_n must be in some class (eq 3). (2) Each

$$\sum_{i=1}^{i=c} a_i = n! \tag{3}$$

of the n ligands must be in some cycle of each permutation in P_n (counting, of course, "fixed points" of cycles of length 1 represented by $x_1^{c_1}$) (eq 4). The cycle indices $Z(P_n)$ for 4

$$\sum_{j=1}^{j=n} jc_{ij} = n \text{ for } 1 \leq i \leq c \tag{4}$$

$\leq n \leq 9$ are given in Table I[24] since these cycle indices are important to the treatment in this paper.

Several basic concepts and definitions of group theory[16,18] will now be reviewed since they are important to the subsequent treatment in this paper. A *subgroup* of a group G is a subset H which is itself a group under the group operation.[16,18] The fact that H is a subgroup of G is written $H \subset G$. If $|G|$ and $|H|$ are the numbers of elements in G and H, respectively, then the quotient $|G|/|H|$ (which must be an integer by Lagrange's theorem[18]) is the *index* of the subgroup H in the group G. If a and x are two elements of group G then $x^{-1}ax$ will be equal to some element of the group, e.g., b. The elements a and b are then said to be *conjugate*.[16] A complete set of elements of a group which are conjugate to one another is called a *class* of the group. A *normal subgroup* N of a group G, written $N \triangleleft G$, is a subgroup which consists only of *entire* conjugate classes of G.[18,23] A *normal chain* of a group G is a sequence of normal subgroups $C_1 \triangleleft N_{a_1} \triangleleft N_{a_2} \triangleleft N_{a_3} \triangleleft \ldots \triangleleft N_{a_s} \triangleleft G$, where s is the number of normal subgroups (besides C_1 and G) in the normal chain. If such a chain starts with the identity group C_1 and leads to G and if all of the quotient groups[18] $N_{a_1}/C_1 = C_{a_1}$, $N_{a_2}/N_{a_1} = C_{a_2}$, ..., $G/N_{a_s} = C_{a_{s+1}}$ are cyclic, then G is a *composite* or *soluble* group. Otherwise G is a *simple group*. A soluble group can be expressed as a *direct product* of the factor groups $C_{a_1} \times C_{a_2} \times \ldots \times C_{a_{s+1}}$.

We can illustrate these group theoretical concepts with some properties of the symmetric permutation groups P_n which will be used in the subsequent sections of this paper. The permutation group P_4 has the normal chain $C_1 \triangleleft C_2 \triangleleft D_2 \triangleleft A_4 \triangleleft P_4$ with the respective quotient groups $C_2/C_1 = C_2$, $D_2/C_2 = C_2$, $A_4/D_2 = C_3$, and $P_4/A_4 = C_2$.[18] The permutation group P_4 can thus be expressed as the direct product $C_2 \times C_2 \times C_3 \times C_2$. The permutation group P_4 is isomorphic to the full tetrahedral group T_d whereas its normal subgroup A_4 of index 2 corresponds to the pure rotational subgroup T. The only normal subgroup of the permutation group P_n ($n \geq 5$) of order $n!$ is the corresponding *alternating group* A_n of index 2 and therefore order $n!/2$. However, A_n ($n \geq 5$) has no normal subgroups. Therefore A_n ($n \geq 5$) is simple and cannot be expressed as a direct product of cyclic subgroups.

Permutations of Three-Dimensional Symmetry Point Groups

In constructing coordination complexes ML_n we are interested in polyhedra in which the vertices representing the n ligands L can be placed on the surface of a sphere with the metal atom at the center of the sphere. In the case of less symmetrical ML_n complexes with different M–L bond distances this sphere may be distorted somewhat to an ellipsoid or an ovoid. However, such a distortion will not alter the topology of the sphere. In other words, the coordination polyhedron of any ML_n complex must be inscribed inside a surface topologically homeomorphic[25] to the sphere so that all of its vertices are located on the surface.

The standard three-dimensional symmetry operations[16] can now be applied to a polyhedron which has n vertices on a sphere or a surface homeomorphic[25] to a sphere. These symmetry operations will be represented by the following terms in the cycle index representing vertex permutations. (1) The identity operation E corresponds to the term x_1^n and always has a coefficient of 1 since any group by definition has a unique identity element.[16,18] This relates to the fact that under the identity operation all vertices remain fixed. (2) The inversion i corresponds to a term $bx_2^{n/2}$ (b is an integer coefficient) and is only possible for a polyhedron with an even number of vertices. No fixed points are possible since a vertex of the polyhedron cannot be located at the center of inversion. (3) A proper rotation C_r can correspond to a term $cx_r^{n/r}$, $cx_1x_r^{(n-1)/r}$, or $cx_1^2x_r^{(n-2)/r}$ (c is a positive integer coefficient) depending upon whether 0, 1, or 2 vertices, respectively, are located on the proper rotation axis. Since a rotation axis can intersect a sphere at only two points, the exponent of x_1 in this term cannot exceed 2. (4) An improper rotation S_r where r is *even* can correspond to a term $dx_r^{n/r}$ or $dx_2x^{(n-2)/r}$ (d is a positive integer coefficient) depending upon whether there is a pair of vertices on the improper rotation axis. Only a single pair of vertices can be on the improper rotation axis because of the topology of the sphere. (5) An improper rotation S_r where r is *odd* can correspond to a term $ex_r^yx_{2r}^z$ or $ex_2x_r^yx_{2r}^w$ (e is a positive integer coefficient) depending upon whether there is a pair of vertices on the odd improper rotation axis. The parameter y refers to the number of rotationally related groups of r points located in the reflection plane of the S_r improper rotation. Furthermore, $ry + 2rz = n$ and $2 + ry + 2rw = n$. The only case where $y \neq 0$ is encountered in this paper is the x_3x_6 term in cycle indices of nine-vertex systems (e.g., the 4,4,4-tricapped trigonal prism[2]) representing an S_3 operation. (6) A reflection plane σ can correspond to a term $fx_1^ax_2^{(n-a)/2}$ (f is a positive integer coefficient), where a is the number of vertices in the reflection plane.

Inspection of the terms in the cycle indices given in Table I for the symmetric groups P_n ($n \geq 6$)[24] indicates that some of the terms (e.g., $40x_1^3x_3$ for P_6) are of none of the above six types. These cycle index terms are thus *forbidden terms* for three-dimensional point groups.

The forbidden terms of the cycle indices may be classified into the following four types. (1) $x_1^ax_r^b$ ($a > 2$, $b \geq 1$, and $r \geq 3$) since no more than two vertices can be on a rotation axis C_r. Thus $70x_1^4x^3$ is a forbidden term in $Z(P_7)$ (Table I) since four vertices (represented by x_1^4) cannot be fixed points in a threefold rotation represented by x_3 (i.e., four points cannot lie on a C_3 axis). (2) $x_2^ax_r^b$ ($a > 1$, $b \geq 1$, and $r \geq 3$) since an improper rotation axis (S_r) can only have zero or

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two collinear vertices. Thus $210x_2^2x_3$ is a forbidden term in $Z(P_7)$ since the threefold improper rotation axis can only have zero or two collinear points. (3) $x_a^px_b^q$ ($a \geq 3$, $b \geq 3$, and $a \neq b$, $2b$, or $b/2$) since the same rotation axis cannot be of different orders. Thus $420x_3x_4$ is a forbidden term in $Z(P_7)$ since the same rotation axis cannot both be a threefold (represented by x_3) and a fourfold (represented by x_4) rotation axis at the same time. (4) $x_1^ax_2^bx_r^c$ (a, b, and $c \neq 0$ and $r \geq 3$) since the same axis cannot be both a proper (C_r) and an improper (S_r) rotation axis at the same time. Thus $630x_1x_2x_4$ is a forbidden term in $Z(P_7)$ since the fourfold axis represented by x_4 cannot simultaneously be a proper (represented by x_1) and an improper (represented by x_2) axis.

A term of the cycle index $Z(P_n)$ that is not a forbidden term in an *allowed term* (relative to realization in three-dimensional space). In Table I t represents the total number of terms in the cycle index $Z(P_n)$ and t^* represents the number of allowed terms. As n rises, t^* rises only slightly so that, for the cases of P_n discussed in this paper ($5 \leq n \leq 9$), $t^* - n = 3 \pm 1$. This indicates that as the number of vertices n of polyhedra is increased, the number of possible families of polyhedra of different symmetries does not rise drastically.

The fact that cycle index terms of the types $x_1^ax_r^b$ and $x_2^cx_r^b$ ($a > 2$, $b \geq 3$, $c > 1$, and $r \geq 3$) are forbidden in three-dimensional point groups leads directly to the following concept of *forbidden axes*: rotation axes C_r and S_r when $n/2 < r < n - 2$ are forbidden for three-dimensional polyhedra with n vertices. Thus a polyhedron with seven vertices cannot have a fourfold C_4 or S_4 rotation axis.

The following more specific features of the three-dimensional point groups[15] are of interest. (1) All of the three-dimensional point groups except for the icosahedral groups I and I_h are isomorphic to direct products[18] of single generator[18] cyclic groups $C_r \times C_s \times \ldots \times C_z$. (2) The symmetric groups P_n ($n \geq 6$) have one or more forbidden terms in their cycle indices (i.e., $t - t^* > 0$). The groups P_n ($n \geq 6$) therefore cannot be isomorphic to three-dimensional point groups. Thus three-dimensional polyhedra with six or more vertices must have fewer than $n!$ symmetry elements (i.e., be of "lower symmetry" than P_n). In practice such polyhedra with n vertices ($n \geq 6$) will be of much lower symmetry than P_n. (3) The symmetric group P_5 has no forbidden terms in its cycle index. However, it cannot be isomorphic to the point group of a polyhedron with five vertices. In terms of graph theory[26] the group P_5 is the automorphism group of the complete graph[26-28] with five vertices (designated as K_5). However, the complete graph K_5 is nonplanar by Kuratowski's theorem[29] and therefore cannot be realized as a three-dimensional polyhedron. (Actually K_5 is the analogue of the tetrahedron in four dimensions.) Nevertheless, the symmetric group P_5 is isomorphic except for realignments of the conjugacy classes to the icosahedral point group I_h permuting a minimum of 12 points.

If $n \geq 5$, a collection of n points with the permutation group P_n (i.e., the automorphism group[28,30] of the nonplanar complete graph K_n) cannot be placed on the surface of the sphere. This collection of n points therefore must be distorted in order for it to fit on the surface of the sphere. In making this distortion of P_n ($n \geq 5$) some of the $n!$ permutations of P_n will be lost to give a smaller permutation group G isomorphic with a realizable three-dimensional point group. Minimally all of the permutations of P_n will be lost which correspond to forbidden terms in its cycle index. In addition, some of the permutations of P_n which correspond to allowed terms in its cycle index may also be lost in order to retain all of the group properties of G. Thus in a crude sense three-dimensional space as represented as points on a surface of a sphere (topological genus zero[31]) is not fully symmetrical. Some distortion of an ensemble of $n \geq 5$ points with the highly symmetrical P_n automorphism groups is necessary for this ensemble to "fit" into three-dimensional space.

The concept of distortion can be given a more precise meaning which is useful for treatments such as those presented in this paper. Thus a process where symmetry elements are removed from a polyhedron with a point group G of order g or a graph with an automorphism group G of order g to give a new less symmetrical figure with a symmetry or automorphism group H of order h ($h < g$) is called a *distortion* if H is a subgroup of G. By Lagrange's theorem[18] the quotient g/h is an integer k which can be called the *index* of the distortion. This paper discusses distortions of P_n which remove the symmetry elements corresponding to forbidden terms in the cycle index $Z(P_n)$.

The essential features of the treatment in this paper for the polyhedral skeletons of the coordination complexes ML_n can be summarized as follows. (1) The t^* terms in the cycle index $Z(P_n)$ of the symmetric group of degree n are selected which are allowed terms for three-dimensional symmetry operations. (2) Sets of these allowed terms are selected in different ways to correspond to actual three-dimensional symmetry point groups $G_1, G_2, \ldots, G_{f_n}$ so that $G_i \subset G_j$ for all $i \neq j$, $1 \leq i$, and $j \leq f_n$, where f_n is the number of families of polyhedra for coordination number n. These point groups $G_1, G_2, \ldots, G_{f_n}$ will represent the fundamental polyhedra in their respective families 1, 2, ..., f_n. These fundamental polyhedra are subject to distortion as defined above to form distorted polyhedra P_i' with lower symmetry point groups G_i' where $G_i' \subset G_i$. Whereas two fundamental polyhedra from different families of n vertex polyhedra cannot have the same point groups (i.e., $G_i \neq G_j$) and even $G_i \not\subset G_j$ and $G_j \not\subset G_i$, distorted polyhedra from different families can have the same point group. (3) Only at this point in the treatment are constraints introduced to limit consideration to chemically feasible polyhedra for ML_n complexes using available M orbitals. In this paper only s, p, and d orbitals are assumed to be available, thereby making 9 the maximum coordination number of M. In some cases distortions of the maximum symmetry polyhedra in a given family may be necessary to generate chemically feasible polyhedra. Thus for coordination number 8 the cube (point group O_h with 48 symmetry elements) must be distorted to the dodecahedron (point group D_{2d} with 8 symmetry elements) before an eight-vertex polyhedron is obtained which can be found by using only metal s, p, and d orbitals. Such hybridization questions can be tested by standard methods of chemical group theory[16] involving the transformation properties of the s, p, and d orbitals. The index of this $O_h \rightarrow D_{2d}$ distortion is $48/8 = 6$, and this distortion essentially involves removal of the threefold symmetry elements of O_h in such a way that the resulting lower symmetry polyhedron can be formed by s, p, and d orbitals. Furthermore, a general rule that arises at this point in the treatment is the inability to construct in ML_n complexes by using only M s, p, and d orbitals any coordination polyhedra with principal proper rotation axes sixfold and higher. Thus within the scope of this treatment polyhedra containing C_6, C_7, and C_8 rotation axes are chemically forbidden even though they may be geometrically and topolog-

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(26) M. Behzad and G. Chartrand, "Introduction to the Theory of Graphs", Allyn and Bacon, Boston, 1971.

(27) R. J. Wilson, "Introduction to Graph Theory", Oliver and Boyd, Edinburgh, 1972, p 16.

(28) N. L. Biggs, "Algebraic Graph Theory", Cambridge University Press, London, 1974.

(29) K. Kuratowski, *Fundam. Math.*, **15**, 271 (1930).

(30) N. L. Biggs, "Finite Groups of Automorphisms", Cambridge University Press, London, 1971.

(31) P. J. Giblin, "Graphs, Surfaces, and Homology", Chapman and Hall, London, 1977, p 66.

Table II. Cycle Index of P_5 and Its Relation to the Symmetry Point Groups of the Maximum Symmetry Five-Vertex Polyhedra

polyhedron	group P_5	$\lvert G\rvert$[a]	cycle index term or corresponding point group symmetry operation						
			x_1^5	$10x_1^3x_2$	$20x_1^2x_3$	$15x_1x_2^2$	$30x_1x_4$	$20x_2x_3$	$24x_5$
trigonal bipyramid	D_{3h}	12	E	$\sigma_h + 3\sigma_v$	$2C_3$	$3C_2'$		$2S_3$	
square pyramid	C_{4v}	8	E	$2\sigma_v$		$C_2 + 2\sigma_d$	$2C_4$		
planar pentagon	D_5	10	E			$5C_2'$			$2C_5 + 2C_5^2$

[a] For group P_5, $\lvert G\rvert = 120$.

Table III. Cycle Index of P_6 and Its Relation to the Cycle Indices of Lower Symmetry Permutation Groups and the Maximum Symmetry Six-Vertex Polyhedra Point Groups

permutation group or polyhedron	$\lvert G\rvert$	cycle index terms										
		x_1^6	$x_1^4x_2$	$x_1^3x_3$	$x_1^2x_2^2$	$x_1^2x_4$	$x_1x_2x_3$	x_1x_5	x_2^3	x_2x_4	x_3^2	x_6
(A) Permutation Groups (Cycle Index Coefficients × $\lvert G\rvert$ Given)												
P_6	720	1	15	40	45	90	120	144	15	90	40	120
$P_3[P_2]$	48	1	3	0	9	6	0	0	7	6	8	8
$P_2[P_3]$	72	1	6	4	9	0	12	0	6	18	4	12
(B) Maximum Symmetry Polyhedra (Corresponding Symmetry Operations Given)												
octahedron ($O_h \approx P_3[P_2]$)	48	E	$3\sigma_h$	X	$3C_2 + 6\sigma_d$	$6C_4$	X		$6C_2' + i$	$6S_4$	$8C_3$	$8S_6$
pentagonal pyramid (C_{5v})	10	E		X	$5\sigma_v$		X	$2C_5 + 2C_5^2$				
(C) Some Further Distortions of the Octahedron												
trigonal prism (D_{3h})	12	E		X	$3\sigma_v$		X		$3C_2' + \sigma_h$		$2C_3$	$2S_3$
square bipyramid (D_{4h})	16	E	$\sigma_h + 2\sigma_v$	X	$C_2 + 2C_2' + 2\sigma_d$	$2C_4$	X		$2C_2'' + i$	$2S_4$		
planar hexagon (D_6)	12	E		X	C_2'		X		$3C_2'' + C_2$		$2C_3$	$2C_6$

ically allowed.

Application to Polyhedra for Coordination Numbers 4–9

A. Coordination Number 4. The cycle index for P_4 has only terms which are allowed for three-dimensional point groups. The permutation group P_4 ($|P_4| = 4! = 24$) is isomorphic with the full point group T_d of the tetrahedron, the usual polyhedron for coordination number 4. The D_4 planar square ($|D_4| = 8$) found, for example, in d^7 and d^8 transition-metal complexes is formed from the tetrahedron by a distortion of index 3 involving twisting of a pair of opposite edges until all four vertices are coplanar. Thus for coordination number 4 there is only a single polyhedron family with the regular tetrahedron as the fundamental polyhedron.

B. Coordination Number 5. The cycle index for P_5, like that for P_4, has only terms which are allowed for three-dimensional point groups. However, as noted above, a five-vertex polyhedron is impossible with a symmetry point group isomorphic to P_5. Thus the P_5 permutation group must be distorted (i.e., some "symmetries" lost by deletion of permutations) before it can represent a symmetry point group realizable in three-dimensional space. This can be done in three different ways as depicted in Table II.

(1) D_{3h} Trigonal Bipyramid (Distortion Index = 120/12 = 10). The fourfold (x_1x_4) and fivefold (x_5) terms are deleted.

(2) C_{4v} Square Pyramid (Distortion Index = 120/8 = 15). The threefold ($x_1^2x_3$ and x_2x_3) and fivefold (x_5) axis terms are deleted.

(3) D_5 Planar Pentagon (Distortion Index = 120/10 = 12). The threefold ($x_1^2x_3$ and x_2x_3) and fourfold (x_1x_4) axis terms are deleted. In addition, precisely three vertices of a planar pentagon cannot be coplanar. Therefore the $x_1^3x_2$ term is forbidden and must also be deleted.

The three families of five-vertex polyhedra thus correspond to deletions of the (4 + 5)-fold, the (3 + 5)-fold, and the (3 + 4)-fold rotations from the full P_5 symmetry. Among these three families of polyhedra for coordination number 5 only the D_5 planar pentagon can lead to five equivalent ligands. However, the planar pentagon is an unfavorable coordination polyhedron for ML$_5$ complexes for the following reasons:[32] (1) excessive interligand repulsion and (2) inability to use all three p orbitals of M (i.e., sp^{2}d^2 rather than sp^{3}d hybridization is required for the planar pentagon). For these reasons the planar pentagon is never found in actual ML$_5$ coordination complexes.[32]

C. Coordination Number 6 (Table III). The cycle index for P_6 ($|G| = 720$) has the forbidden terms $40x_1^3x_3$ and $120x_1x_2x_3$ and thus cannot represent a three-dimensional point group. Thus P_6 must be distorted to remove at least the permutation symmetries represented by these forbidden terms before a point group is obtained suitable for a six-vertex polyhedron. The octahedron (O_h with $|G| = 48$) comes remarkably close to achieving this objective since its cycle index contains all of the terms of that of P_6 except for the two forbidden terms $x_1^3x_3$ and $x_1x_2x_3$ and the allowed term x_1x_5 representing a fivefold rotation axis. Thus *all* six-vertex polyhedra except for the single possible polyhedron containing a fivefold rotation axis (the C_{5v} pentagonal pyramid) can be obtained by distorting the octahedron as exemplified by the following cases.

(1) D_{3h} Trigonal Prism (Distortion Index = 48/12 = 4). An opposite pair of (triangular) faces of the octahedron is rotated 120° relative to each other thereby removing the fourfold axis terms $x_1^2x_4$ and x_2x_4 corresponding to C_4 and S_4 operations, respectively.

(2) D_{4h} Square Bipyramid (Distortion Index = 48/16 = 3). An opposite pair of vertices of the octahedron is stretched thereby removing the three- and sixfold axis terms corresponding to the C_3 (i.e., x_3^2) and S_6 (i.e., x_6) operations, respectively.

(3) D_6 Planar Hexagon (Distortion Index = 48/12 = 4). An opposite pair of faces of the octahedron is squashed until all six vertices lie in the same plane. This squashing operation removes the fourfold axis $x_1^2x_4$ and x_2x_4 as well as the $x_1^4x_2$ terms requiring precisely four coplanar vertices (see the discussion above on the planar pentagon).

There are thus only two families of six-vertex polyhedra: (a) the octahedron from which all chemically interesting ML$_6$ coordination polyhedra can be derived through appropriate distortions[33] and (b) the pentagonal pyramid which is the

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[32] E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967).

[33] D. L. Kepert, *Prog. Inorg. Chem.*, **23**, 1 (1977).

Table IV. Allowed Terms of the Cycle Index of P_7 for Three-Dimensional Symmetry Point Groups and Their Relation to the Maximum Symmetry Seven-Vertex Polyhedra Point Groups

		allowed cycle index terms of P_7 and corresponding symmetry operations								
polyhedron	$\|G\|$	x_1^7	$21x_1^5x_2$	$105x_1^3x_2^2$	$504x_1^2x_5$	$105x_1x_2^3$	$280x_1x_3^2$	$840x_1x_6$	$504x_2x_5$	$720x_7$
pentagonal bipyramid (D_{5h})	20	E	σ_h	$5\sigma_v$	$2C_5 + 2C_5^2$	$5C_2'$			$2S_5 + 2S_5^3$	
hexagonal pyramid (C_{6v})	12	E		$3\sigma_d$		$C_2 + 3\sigma_d$	$2C_3$	$2C_6$		
planar heptagon (D_7)	14	E				$7C_2'$				$2C_7 + 2C_7^2 + 2C_7^3$

unique six-vertex polyhedron not belonging to the octahedral family. Since the pentagonal pyramid is of no importance in the chemistry of ML_6 coordination complexes, all six-coordinate polyhedra can be derived from the octahedron through appropriate distortions. Thus an octahedron of symmetry O_h with only 48 symmetry elements is as effective as the P_6 symmetric group with 6! = 720 symmetry elements in exhibiting all of the symmetries possible for six-coordinate polyhedra of chemical relevance. The reason for this is that the symmetry lost in reducing P_6 symmetry to O_h symmetry represents mainly operations that are impossible in three-dimensional space (i.e., those corresponding to the $x_1^3x_3$ and $x_1x_2x_3$ forbidden cycle index terms).

The point group of the octahedron is an example of a *wreath product* permutation group.[21,22,24,34,35] Consider a fully symmetric permutation group P_n where $n = ab$ and a and b are positive integers other than 1. The wreath product $P_a[P_b]$ of order $|G| = a!(b!)^a$ involves splitting the n objects into a sets of b objects each. The $b!$ permutations of P_b can be applied independently to each of the a sets of b objects, hence the factor $(b!)^a$ in $|G|_{P_a[P_b]}$. In addition, the a sets of b objects can be exchanged according to the $a!$ permutations in P_a leading to the factor $a!$ in $|G|_{P_a[P_b]}$. The wreath products $P_a[P_2]$ represent the symmetries of the a-dimensional analogues of the cube or its dual analogous to the octahedron in three-dimensional space (also[3] called the a-dimensional "cross-polytope") or the automorphism groups of the hyperoctahedral graphs[28] H_a. The wreath products $P_2[P_b]$ represent the automorphism groups (i.e., the symmetries) of the $K_{b,b}$ bipartite graphs[26] which are nonplanar (i.e., cannot correspond to a three-dimensional polyhedron) for $b \geq 3$. The splitting of P_n into the wreath product $P_a[P_b]$ ($ab = n$) removes some of the permutations in P_n (i.e., reduces the "symmetry" of the system). However, if the lost permutations are irrelevant to the problem at hand, the wreath product splitting of P_n into $P_a[P_b]$ ($ab = n$) represents a simplification since the size of the group which must be treated is reduced. Obviously if n is prime (e.g., 5 or 7), P_n cannot be split into a wreath product $P_a[P_b]$.

Table III shows the cycle indices not only for P_6 but also for the two possible wreath products $P_3[P_2]$ and $P_2[P_3]$ permuting six objects. The wreath product $P_3[P_2]$ corresponds to the ordinary octahedral point group O_h and has been discussed above. The other wreath product $P_2[P_3]$ is the automorphism group of the $K_{3,3}$ bipartite graph. Reduction of the symmetry from P_6 to $P_2[P_3]$ removes the proper four- and fivefold axis cycle index terms $x_1^2x_4$ and x_1x_5 and retains the useless forbidden terms $x_1^3x_3$ and $x_1x_2x_3$. Thus in studying coordination polyhedra symmetry reduction of P_6 to $P_2[P_3]$ deletes important permutations and retains unimportant permutations whereas symmetry reduction of P_6 to $P_3[P_2]$ deletes unimportant permutations and retains important permutations.

D. Coordination Number 7 (Table IV). Only nine of the 15 terms in the cycle index for P_7 ($|G|$ = 7! = 5040) are allowed for three-dimensional point groups. Distortion of the P_7 permutation group with removal of at least the forbidden symmetries leads to three families of seven-vertex polyhedra derived from the following fundamental polyhedra.

(1) D_{5h} Pentagonal Bipyramid (Distortion Index = 5040/20 = 252). The threefold ($x_1x_3^2$ and x_1x_6) and sevenfold (x_7) axis terms are deleted. In an ML_7 complex this polyhedron can be formed by using only the metal s, p, and d orbitals[2] and is frequently found in actual metal complexes.[5] Further distortion of the pentagonal bipyramid to destroy the fivefold axis can lead to the various C_{2v} seven-vertex coordination polyhedra.[2,5] The distortion index from D_{5h} to C_{2v} is 20/4 = 5.

(2) C_{6v} Hexagonal Pyramid (Distortion Index = 5040/12 = 420). The fivefold $x_1^2x_5$ and x_2x_5) and sevenfold (x_7) axis terms are deleted. Since precisely five vertices cannot be coplanar, the $x_1^5x_2$ term also disappears. The six coplanar ligands make the hexagonal pyramid not only unfavorable because of excess interligand repulsion energy but impossible to form by using only s, p, and d orbitals of the central metal. However, distortion of the six coplanar ligands of the hexagonal bipyramid into two sets of three ligands thereby destroying the sixfold axis but retaining the threefold axis leads to the C_{3v} capped octahedron. The capped octahedron is one of the more favorable seven-coordinate polyhedra[5] since it has a relatively low interligand repulsion energy and can be formed by metal s, p, and d orbitals.

(3) D_7 Planar Heptagon (Distortion Index = 5040/14 = 360). The threefold ($x_1x_3^2$ and x_1x_6) and fivefold ($x_1^2x_5$ and x_2x_5) axis terms are deleted. Restrictions on the number of coplanar vertices also cause the terms $x_1^5x_2$ and $x_1^3x_2^2$ to disappear. Although the planar heptagon is the only configuration leading to seven equivalent ligands in an ML_7 complex, excessive interligand repulsion and inability to be formed by a reasonable set of metal atomic orbitals prevent the planar heptagon from playing any role in the chemistry of seven-coordinate complexes.[5]

The following additional features of seven-vertex polyhedra are noted. (1) Seven is the smallest integer n for which an integer, namely, 4, falls between $n/2$ and $n - 2$. A fourfold axis is therefore forbidden in a seven-vertex polyhedron. (2) Since 7 is a prime number, wreath products cannot be found which represent permutations on seven objects. Therefore wreath products cannot be used to generate a permutation group which is a proper subgroup of P_7 and of which the symmetry point groups of all chemically relevant seven-vertex polyhedra are subgroups.

E. Spanning Subgroups of the Symmetric Permutation Groups. As n increases above 6, the order of the symmetric group P_n, $n!$, becomes inconveniently large (7! = 5040, 8! = 40 320, etc.) and the cycle indices (Table I) contain increasing numbers of terms. Fortunately, the situation is not as complicated as it might seem since, as n increases above 6, increasing fractions of the terms in $Z(P_n)$ become forbidden for operations in three-dimensional symmetry point groups. However, further simplification can be achieved if subgroups of P_n, designated generically as Q_n, can be found so that all symmetry point groups of chemically significant coordination polyhedra with n vertices are subgroups of Q_n; i.e., the permutations of Q_n *span* all of those found in the desired set of polyhedra with n vertices. Such subgroups Q_n of P_n are of particular interest when the forbidden cycle index terms of

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(34) H. Bechtell, "Theory of Groups", Addison-Wesley, Reading, Mass., 1971, Chapter 3.

(35) J. G. Nourse and K. Mislow, *J. Am. Chem. Soc.*, **97**, 4571 (1975).

P_n are removed without sacrificing any of the important allowed cycle index terms of P_n. In general, the only *allowed* cycle index terms of P_n which are acceptable sacrifices in forming a suitable subgroup Q_n are higher fold proper rotation axis terms (particulary $x_1^a x_r$, where $a = 1$ or 2 and $r > 6$) which require so many coplanar ligands that corresponding coordination polyhedra have excessive interligand repulsion. We have seen above how the octahedral group O_h, representable also as the wreath product $P_3[P_2]$, is a nearly ideal Q_6 since all of the forbidden cycle index terms of P_6 are removed while sacrificing only the allowed term x_1x_5.

Table V summarizes the properties of subgroups of P_n ($6 \leq n \leq 9$) which have been investigated as possible spanning subgroups Q_n for the point groups of three-dimensional polyhedra with n vertices. The cycle indices of these subgroups of P_n in Table V have been divided into allowed and forbidden terms for three-dimensional symmetry operations. In addition, allowed terms in the cycle indices of the fully symmetrical permutation groups P_n which are absent in the cycle indices of the corresponding subgroups Q_n are listed in Table V. A group Q_n will be an effective spanning subgroup of P_n for symmetry point groups of n vertex polyhedra if the following conditions are satisfied. (1) Its cycle index $Z(Q_n)$ contains the minimum number of forbidden terms. (2) The allowed terms in the cycle index of P_n which are absent in that of Q_n represent symmetry operations which are unimportant in chemically significant polyhedra (e.g., sevenfold rotation axes). (3) The group Q_n is *transitive*;[30] i.e., there are one or more operations in Q_n that will permute any of the n objects into any other of the n objects. Thus a set of n objects can be found which has a single *orbit*[30] under the action of Q_n. For example, the group D_{3h} is *not* a transitive permutation group on the five vertices of the trigonal bipyramid since no operation in D_{3h} can interchange apical and equatorial vertices. Thus the vertices of the trigonal bipyramid form two orbits under the action of D_{3h}: the two apical vertices and the three equatorial vertices.

If for a given P_n symmetric permutation group an effective spanning subgroup Q_n can be found, then use of the more limited symmetries of the Q_n subgroup rather than the full symmetries of P_n can have the following advantages. (1) The smaller size of Q_n simplifies manipulations that may be necessary in some cases (e.g., lowers isomer counts[13] in the consideration of stereochemically nonrigid polyhedra). (2) In most cases Q_n is soluble (composite) and therefore corresponds to a direct product of cyclic groups $C_{a_1} \times C_{a_2} \times ... \times C_{a_{s+1}}$, where s is the number of normal subgroups in the normal chain of Q_n (excluding C_1 and Q_n). However, $P_n = A_n \times C_2$ and A_n is simple for $n \geq 5$. The ability to express a composite Q_n as a direct product of cyclic groups may be important in the treatment of nonrigid polyhedra[36,37] where some of the cyclic factor groups of Q_n (i.e., $C_{a_1} \times C_{a_2} \times ... \times C_{a_p}$, where p is the number of normal subgroups in the normal chain of the symmetry point group of the n-vertex polyhedron in question) represent the symmetry of a rigid polyhedron and the remaining cyclic factor groups of Q_n (i.e., $C_{a_{p+1}} \times C_{a_{p+2}} \times ... \times C_{a_{s+1}}$) represent permutation isomerization (fluxional) processes.[36,37]

The use of Q_n rather than the full symmetry of P_n to treat permutational problems such as those involving coordination polyhedra appears to be vaguely analogous to using the proper rotational subgroups T, O, and I instead of their full polyhedral point groups T_d, O_h, and I_h containing also improper rotation axes (including reflection planes).

The success in using the wreath product group $P_3[P_2]$ ($|G| = 48$) corresponding to the octahedron instead of P_6 ($|G| = 720$) as a Q_6 for generating six-coordinate polyhedra suggests the use of wreath product groups to represent the important permutations in eight- and nine-vertex polyhedra. For eight-vertex polyhedra the hyperoctahedral wreath product $P_4[P_2]$ (Table V) is similarly effective as a Q_8 for the following reasons. (1) Only three of the 14 terms in its cycle index represent permutations forbidden for three-dimensional point groups. (2) The only allowed term in $Z(P_8)$ which is missing in $Z(P_4[P_2])$ is x_1x_7. Thus the only polyhedron which is lost by using $P_4[P_2]$ with $|G| = 384$ instead of P_8 with $|G| = 40320$ is the chemically unimportant heptagonal pyramid. This is a negligible price to pay for reducing the size of the permutation group by a factor of 105.

The bipartite wreath product $P_2[P_4]$ is a much less effective Q_8 than the hyperoctahedral wreath product $P_4[P_2]$ for the following reasons. (1) $Z(P_2[P_4])$ has twice the number of forbidden terms as compared with $Z(P_4[P_2])$. (2) $Z(P_2[P_4])$ is missing not only an allowed x_1x_7 term corresponding to a heptagonal pyramid but also allowed $x_1^2x_6$ and $x_2x_3^2$ terms corresponding to more important eight-coordination polyhedra such as the hexagonal bipyramid and the bicapped octahedron. (3) $P_2[P_4]$ is much larger ($|G| = 1152$) than $P_4[P_2]$ ($|G| = 384$).

For the nine-vertex polyhedra the group $P_3[P_3]$ is the only possible wreath product involving nine vertices. It, however, is a very poor Q_9 for the following reasons. (1) Its cycle index $Z(P_3[P_3])$ has a larger number (10) of forbidden terms as compared with only nine allowed terms. (2) Its cycle index $Z(P_3[P_3])$ is missing not only the unimportant sevenfold ($x_1^2x_7$ and x_2x_7) and eightfold (x_1x_8) axis terms but also the much more important fourfold axis term $x_1x_4^2$.

The use of wreath products thus provides the effective octahedral and hyperoctahedral spanning subgroups $P_3[P_2]$ and $P_4[P_2]$, respectively, for six- and eight-vertex polyhedra but does not generate useful spanning subgroups Q_7 and Q_9 for seven- and nine-vertex polyhedra.

Other approaches have also been investigated for the generation of effective spanning subgroups Q_9 and Q_7 of P_9 and P_7, without using wreath products. For generation of an effective Q_9 the *line graph* $L(K_{3,3})$ is generated from the bipartite graph $K_{3,3}$ by the standard procedure[28] involving taking the nine edges of $K_{3,3}$ as the vertices of $L(K_{3,3})$ and joining these nine vertices with a total of 18 edges so that two vertices of $L(K_{3,3})$ have an edge between them whenever the corresponding edges in $K_{3,3}$ have a common vertex. The line graph $L(K_{3,3})$ is identical with the hyperpentagonal graph[38] C_5^4. Since forming a line graph does not add or subtract symmetry elements from the original graph, the automorphism group of $L(K_{3,3})$ will be the same as that of $K_{3,3}$. However, the cycle index of the line graph $Z(L(K_{3,3}))$ will be different from that of the original graph $Z(K_{3,3})$ since $Z(L(K_{3,3}))$ (designated[24] as the *pair group* $Z(P_2[P_3]^{(2)})$ will consist of the permutations of the nine edges of $K_{3,3}$ (i.e., connected vertex pairs) rather than the six vertices.

Table V shows that $P_2[P_3]^{(2)}$ is an excellent group to use for Q_9. Although it has only 72 elements, its cycle index contains no forbidden terms and among allowed terms lacks only seven-, eight- and ninefold axis terms ($x_1^2x_7$, x_1x_8, x_2x_7, x_9) as well as terms corresponding to relatively large numbers of fixed points imposing unreasonable coplanarity requirements ($x_1^7x_2$, $x_1^5x_2^2$). The pair wreath product group $P_2[P_3]^{(2)}$ will therefore be used below instead of the full permutation group P_9 for treating nine-vertex polyhedra appropriate for nine-coordinate complexes.

The seven-vertex system is not amenable to an analogous treatment. Thus it is impossible to find an effective $Q_7 \subset P_7$

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(36) H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963).

(37) C. M. Woodman, *Mol. Phys.*, **19**, 753 (1970).

(38) R. B. King, *Houston J. Math.*, **5**, 209 (1979).

Table V. Some Subgroups of P_n ($6 \leq n \leq 9$) Investigated as Possible Candidates for Subgroups Q_n Spanning Symmetry Point Groups of Coordination Polyhedra with n Vertices

group Q_n	$\lvert Q_n \rvert$	cycle index of Q_n (multiplied by $\lvert Q_n \rvert$)		allowed terms in $Z(P_n)$ which are absent in $Z(G)$
		allowed terms	forbidden terms	
		(A) Permutations on Six Vertices		
$P_3[P_2]$	48	$x_1^6 + 3x_1^4x_2 + 9x_1^2x_2^2 + 6x_1^2x_4 + 7x_2^3 + 6x_2x_4 + 8x_3^2 + 8x_6$		x_1x_5
$P_2[P_3]$	72	$x_1^6 + 6x_2^4x_2 + 9x_1^2x_2^2 + 6x_2^3 + 18x_2x_4 + 4x_3^2 + 12x_6$	$4x_1^3x_3 + 12x_1x_2x_3$	$x_1^2x_4, x_1x_5$
		(B) Permutations on Seven Vertices		
$PSL(2,7)$	168	$x_1^7 + 21x_1^3x_2^2 + 56x_1x_3^2 + 48x_7$	$42x_1x_2x_4$	$x_1^5x_2, x_1^2x_5, x_1x_6, x_2x_5$
		(C) Permutations on Eight Vertices		
$P_4[P_2]$	384	$x_1^8 + 4x_1^6x_2 + 18x_1^4x_2^2 + 28x_1^2x_2^3 + 32x_1^2x_3^2 + 32x_1^2x_6 + 25x_2^4 + 32x_2x_3^2 + 32x_2x_6 + 60x_4^2 + 48x_8$	$12x_1^4x_4 + 24x_1^2x_2x_4 + 36x_2^2x_4$	x_1x_7
$P_2[P_4]$	1152	$x_1^8 + 12x_1^6x_2 + 42x_1^4x_2^2 + 36x_1^2x_2^3 + 64x_1^2x_3^2 + 33x_2^4 + 180x_2^2x_4 + 192x_2x_6 + 108x_4^2 + 144x_8$	$16x_1^5x_3 + 12x_1^4x_4 + 96x_1^3x_2x_3 + 72x_1^2x_2x_4 + 48x_1x_2^2x_3 + 96x_1x_3x_4$	$x_1^2x_6, x_1x_7, x_2x_3^2$
		(D) Permutations on Nine Vertices		
$P_3[P_3]$	1296	$x_1^9 + 9x_1^7x_2 + 27x_1^5x_2^2 + 45x_1^3x_2^3 + 12x_1^3x_3^2 + 54x_1x_2^4 + 80x_3^3 + 288x_3x_6 + 144x_9$	$6x_1^6x_3 + 36x_1^4x_2x_3 + 54x_1^3x_2x_4 + 54x_1^2x_2^2x_3 + 36x_1^3x_6 + 162x_1x_2^2x_4 + 36x_1x_2x_3^2 + 108x_1x_2x_6 + 36x_2^3x_3 + 108x_2x_3x_4$	$x_1^2x_7, x_1x_4^2, x_1x_8, x_2x_7$
$P_2[P_3]^{(2)}$	72	$x_1^9 + 12x_1^3x_2^3 + 9x_1x_2^4 + 18x_1x_4^2 + 8x_3^3 + 24x_3x_6$		$x_1^7x_2, x_1^5x_2^2, x_1^2x_7, x_1x_8, x_2x_7, x_9$

Table VI. Allowed Terms of the Cycle Index of $P_4[P_2]$ for Three-Dimensional Point Groups and Their Relation to the Symmetry Point Groups of the Maximum Symmetry Eight-Vertex Polyhedra

polyhedron	group	$\lvert G \rvert$	allowed cycle index terms of $P_4[P_2]$ and corresponding symmetry operations										
			x_1^8	$4x_1^6x_2$	$18x_1^4x_2^2$	$28x_1^2x_2^3$	$32x_1^2x_3^2$	$32x_1^2x_6$	$25x_2^4$	$32x_2x_3^2$	$32x_2x_6$	$60x_4^2$	$48x_8$
hexagonal bipyramid	D_{6h}	24	E	σ_h	$3\sigma_v$	$C_2 + 3C_2' + 3\sigma_d$	$2C_3$	$2C_6$	$3C_2' + i$	$2S_3$	$2S_6$		
square antiprism	D_{4d}	16	E			$4C_2' + 4\sigma_d$			C_2			$2C_4$	$2S_8 + 2S_8^3$
cube	O_h	48	E		$6\sigma_d$		$8C_3$		$3C_2 + i + 3\sigma_h + 6C_2'$		$8S_6$	$6C_4 + 6S_4$	

Table VII. Cycle Index of $P_2[P_3]^{(2)}$ and Its Relation to the Symmetry Point Groups of the Maximum Symmetry Nine-Vertex Polyhedra

polyhedron	group	$\lvert G \rvert$	cycle index terms and corresponding symmetry operation					
			x_1^9	$12x_1^3x_2^3$	$9x_1x_2^4$	$18x_1x_4^2$	$8x_3^3$	$24x_3x_6$
3,3,3-tricapped trigonal prism	D_{3h}	12	E	$\sigma_h + 3\sigma_v$	$3C_2'$		$2C_3$	$2S_3$
4-capped square antiprism	C_{4v}	8	E	$2\sigma_v + 2\sigma_d$	C_2	$2C_4$		

meeting the above criteria not only because 7 is a prime number (thereby excluding wreath product formation) but also because there are no suitable distance-transitive[28,33] seven-vertex graphs with an automorphism group suitable for Q_7. An "exotic" group which was considered as a possibility for Q_7 is the group $PSL(2,7)$ containing 168 elements[30] which arises in the following contexts: (1) the smallest simple group which is not an alternating group A_n;[39] (2) the automorphisms of the group $C_2 \times C_2 \times C_2$ containing eight elements;[18] (3) the number of different ways of labeling the vertices of a rectangular solid;[18] (4) the group of collineations in a projective plane with seven points.[18,30] However, the cycle index of $PSL(2,7)$ (Table V)[40] contains no $x_1{}^2x_5$ or x_2x_5 terms corresponding to the fivefold axis of the pentagonal bipyramid, a very important polyhedron for seven-coordinate ML_7 complexes. Therefore, $PSL(2,7)$ is unsuitable for a Q_7.

F. Coordination Number 8 (Table VI). As noted above a suitable Q_8 for coordination number 8 is the hyperoctahedral wreath product $P_4[P_2]$ ($|G| = 384$) which is smaller by a factor of 105 relative to the fully symmetrical P_8 ($|G| = 40320$). The only allowed cycle index term in $Z(P_8)$ sacrificed in $Z(P_4[P_2])$ is x_1x_7, but the heptagonal pyramid corresponding to this term is chemically unfeasible. Furthermore, a fivefold axis is forbidden for polyhedra with eight vertices since $8/2 = 4 < 5 < 6 = 8 - 2$. Further distortions of $P_4[P_2]$ can lead to three families of actual eight-coordinate polyhedra with the following maximum symmetry polyhedra.

(1) D_{6h} Hexagonal Bipyramid (Distortion Index = 384/24 = 16). The fourfold axis terms ($x_4{}^2$ and x_8) are deleted from $Z(P_4[P_2])$. However, in an ML_8 complex the hexagonal bipyramid cannot be formed solely by the s, p, and d orbitals of M even if it is distorted further to the D_{3h} bicapped octahedron.

(2) D_{4d} Square Antiprism (Distortion Index = 384/16 = 24). The threefold axis terms ($x_1{}^2x_3{}^2$, $x_1{}^2x_6$, $x_2x_3{}^2$, x_2x_6) are deleted from $Z(P_4[P_2])$. Also since six vertices cannot be coplanar, the $x_1{}^6x_2$ term also disappears from $Z(P_4[P_2])$. The square antiprism *can* be formed solely by metal s, p, and d orbitals in an ML_8 complex and is one of the favored polyhedra for coordination number 8.[6]

(3) O_h Cube (Distortion Index = 384/48 = 8). The sixfold ($x_1{}^2x_6$) and eightfold (x_8) axis terms are deleted from $Z(P_4[P_2])$. Some other terms ($x_1{}^6x_2$, $x_1{}^2x_2{}^3$, and $x_2x_3{}^2$) also disappear which involve odd numbers of transpositions (i.e., an *odd* number of cycles of *even* length). In fact, the cycle index of the cube contains precisely those terms of $Z(P_4[P_2])$ which have an even number (including zero) of cycles of even length (i.e., the sum of the exponents of the x_2, x_4, x_6, and x_8 factors is an even number). The cube *cannot* be formed by using solely metal s, p, and d orbitals in an ML_8 complex. However, further distortion of the cube to remove all threefold axis terms (i.e., $x_1{}^2x_3{}^2$ and x_2x_6) leads to the D_{2d} 8,18,12-dodecahedron[2] (distortion index from the cube = 48/8 = 6), which *can* be formed solely from metal s, p, and d orbitals and is one of the favored polyhedra for coordination number 8.[6]

The three families of eight-vertex polyhedra derived by distortion of the hyperoctahedral wreath product $P_4[P_2]$ thus correspond to deletions of the fourfold, the threefold, and the odd permutations from the $P_4[P_2]$ symmetry. Also note that the D_{4d} point group of the square antiprism has operations of period 8 ($2S_8$ and $2S_8{}^3$) and thus is *not* a subgroup of O_h which has no operations of period 8.

This treatment in this paper thus indicates for the first time the following three-step *distortion chain* of the fully symmetric P_8 group ($|G| = 40320$) to the D_{2d} point group ($|G| = 8$) of the dodecahedron frequently found in eight-coordinate complexes.[6]

(1) Distortion of P_8 to $P_4[P_2]$ (Distortion Index = 40320/384 = 105). This first step of the distortion chain generates a suitable spanning subgroup Q_8 retaining all of the possible symmetries for chemically reasonable eight-vertex polyhedra.

(2) Distortion of $P_4[P_2]$ to O_h (Distortion Index = 384/48 = 8). This second step of the distortion chain generates the maximum possible symmetry for an eight-vertex three-dimensional polyhedron.

(3) Distortion of O_h to D_{2d} (Distortion Index = 48/8 = 6). The final step of this distortion chain generates the maximum subgroup of O_h, namely, D_{2d}, that can correspond to the symmetries of an eight-vertex polyhedron which in an ML_8 complex can be formed by the s, p, d, orbitals of the center M atom.

This distortion chain can be represented schematically as eq 5, where the numbers above the arrows correspond to the indices of the respective distortions. The total index of distortion in this three-step distortion chain is 105 × 8 × 6 = 5040 =7!.

$$P_8 \xrightarrow{105} P_4[P_2] \xrightarrow{8} O_h \xrightarrow{6} D_{2d} \tag{5}$$

G. Coordination Number 9 (Table VII). For coordination number 9 the pair group $P_2[P_3]^{(2)}$ ($|G| = 72$) is used rather than P_9 ($|G| = 362880$) as discussed above. We thus reduce the size of the spanning group by a factor of 5040 = 7! while sacrificing only all of the forbidden terms, the seven-, eight-, and ninefold axis terms, and terms with five and seven fixed points. Furthermore, fivefold axes are forbidden for polyhedra with nine vertices (i.e., $9/2 < 5 < 7$). In addition, the only allowed P_9 cycle index term for nine-vertex polyhedra with period 6 is x_3x_6 corresponding to the improper rotation S_3 as found, for example, in the 4,4,4-tricapped trigonal prism.[2]

After exclusion of the nine-vertex polyhedra with seven-, eight-, and ninefold proper rotation axes (which are eliminated anyway in the drastic distortion from P_9 to $P_2[P_3]^{(2)}$) there remain only the following two families of nine-vertex polyhedra with the following maximum symmetry polyhedra.

(1) D_{3h} 4,4,4-Tricapped Trigonal Prism (Distortion Index = 72/12 = 6). The fourfold axis term $x_1x_4{}^2$ is deleted from $Z(P_2[P_3]^{(2)})$.

(2) C_{4v} 4-Capped Square Antiprism (Distortion Index = 72/8 = 9). The threefold axis terms $x_3{}^3$ and x_3x_6 are deleted from $Z(P_2[P_3]^{(2)})$.

Both of these nine-vertex polyhedra have appropriate symmetries to arise from sp^3d^5 hybridization of the M atom in an ML_9 complex.[2]

Summary

This paper shows how the tendency to use maximum symmetry feasible coordination polyhedra pervades coordination chemistry. However, the requirement of chemical as well as geometrical feasibility is very significant and can lead to major symmetry reduction. A notable example of this is the frequent occurrence of the D_{2d} dodecahedron in eight-coordinate ML_8 complexes. The techniques outlined in this paper involving the cycle indices of the symmetrical group P_n and appropriate wreath product subgroups of P_n for composite n provide an effective method for generating coordination polyhedra without using some of the more difficultly justifiable assumptions of the earlier work.[2] However, the need is still retained for the earlier topological principles[2] for investigating the properties of the resulting polyhedra including particularly the relationships between the numbers and types of vertices, edges, and faces for polyhedra of given symmetry.

An additional result from the treatment in this paper is the discovery that the subgroup Q_n of the fully symmetrical group P_n which contains all of the point groups of chemically im-

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(39) L. E. Dickson, "Linear Groups", Teubner, Leipzig, 1901, pp 309, 310.

(40) F. Klein, *Math. Ann.*, **14**, 428 (1879).

portant polyhedra with n vertices can often be surprising small, particularly when $|Q_n|$ is considered relative to $n!$. For example, a group $Q_9 = P_2[P_3]^{(2)}$ with only 72 elements has been found which spans the symmetries of all of the chemically feasible nine-vertex polyhedra just as well as the much larger group P_9 with 9! = 362 880 elements. It thus appears that use of the Q_n subgroups rather than the fully symmetrical P_n group might offer some advantages of simplicity in depiciting isomerization processes in stereochemically nonrigid polyhedra. Applications of these principles to permutational isomerisms in eight-coordinate ML_8 complexes are currently under investigation.

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Pure- and Mixed-Crystal Optical Studies of the Jahn–Teller Effect for the d^6 Hexafluoroplatinate(IV) Ion

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Measurements have been made of the low-temperature luminescence and Raman spectra of pure Cs_2PtF_6 crystals and Cs_2PtF_6–Cs_2GeF_6 crystals in which PtF_6^{2-} is doped into the Cs_2SiF_6 lattice. In both environments, the Raman spectra at liquid-helium temperature show sharp lines assigned to the a_{1g}, e_g, and t_{2g} internal modes of the PtF_6^{2-} ion. A comparison of the low-temperature Raman and sharp-line luminescence spectra indicates that in the luminescence spectra a Jahn–Teller e_g-type progression occurs with a small degree of anharmonicity present. The luminescence can be assigned as a transition from the $t_{2g}^5e_g$ $\Gamma_3(^3T_{1g})$ twofold degenerate excited electronic state to the t_{2g}^6 $\Gamma_1(^1A_{1g})$ nondegenerate ground electronic state.

Introduction

MX_6^{2-} octahedral hexahalide systems, where M is a 5d transition-metal element, have been the subject of numerous optical studies in recent years.[1] The optical measurements have almost always been mixed-crystal experiments in which the MX_6^{2-} impurity ion is doped in a cubic host such as Cs_2ZrCl_6, Cs_2ZrBr_6, or Cs_2SiF_6 and the optical spectrum is recorded at liquid-helium temperature. It is important to compare the pure-crystal spectra with the impurity ion results. In this paper we report Raman and luminescence experiments for the d^6 PtF_6^{2-} ion in the pure Cs_2PtF_6 case and in the case where the PtF_6^{2-} ion is doped in a host lattice. In particular, the d^6 PtF_6^{2-} ion is an excellent ion to study for two reasons: (1) the PtF_6^{2-} ion in both the pure- and mixed-crystal environments shows strong structured luminescence spectra; (2) the Raman spectra in both the pure and mixed crystals show lines due to the Raman-active a_{1g}, e_g, and t_{2g} modes of the PtF_6^{2-} moiety.

In a previous publication on the PtF_6^{2-} ion,[2] the luminescence spectra were assigned to an a_{1g} progression because of limited data. In these current studies the luminescence spectra were recorded with an infrared optical system and Raman spectra measured at liquid-helium temperature. Also, lifetime studies have been performed in both the pure- and mixed-crystal cases as a function of temperature. Comparison of the luminescence and Raman spectra now leads to a model in which in the luminescence spectra an e_g Jahn–Teller-active progression occurs. The decreasing spacing between the luminescence peaks with decreasing energy is explained by a small degree of anharmonicity in the ground-electronic-state potential surface for the e_g mode.

Experimental Section

The synthesis of Cs_2PtF_6 and the growing of crystals (Cs_2PtF_6, Cs_2PtF_6–Cs_2SiF_6, Rb_2PtF_6–Rb_2SiF_6) have been discussed previously.[2] The analysis of the Rb_2PtF_6–Rb_2SiF_6 and Cs_2PtF_6–Cs_2SiF_6 mixed crystals was carried out by R. W. Stoenner of the Chemistry Department at Brookhaven. The percent Pt was determined by a flameless-graphite-furnace atomic absorption at 2800 °C by standard addition. The percent Si was determined spectrophotometrically with a Cary Model 16 by using the method of Andrew[3] in which ammonium molybdate complexes with silicon to give an absorption band at 810 nm. The results for the actual crystal batch used for the Raman studies showed that for the Rb_2PtF_6–Rb_2SiF_6 mixed crystals the relative amount of Rb_2PtF_6 was 1.3% while for the Cs_2PtF_6–Cs_2SiF_6 crystals the relative amount of Cs_2PtF_6 was 7.9%.

The emission studies were performed by exciting the crystal samples with a Molectron UV 14 nitrogen laser. The resulting luminescence was analyzed with a McPherson 1-m Model 2051 monochromator and a Products for Research TE-241-RF photomultiplier tube. Emission spectra were recorded after amplification of the signal with a PAR 124A lock-in amplifier. Lifetime measurements were made with a PAR boxcar averager, Model 162. In all cases the sample temperatures were obtained with an Lt-3-110 liquid-helium transfer Heli-Tran.

Raman measurements were made with the use of a krypton ion laser excitation at 476.2, 530.9, and 568.2 nm. The details of the detection system have been published.[4] The absorption measurements at liquid-helium temperature were performed with a Cary 17D spectrophotometer.

Results

Emission Spectra. Luminescence measurements were made on single crystals of Cs_2PtF_6, Cs_2PtF_6–Cs_2SiF_6, Cs_2PtF_6–Cs_2GeF_6, and Rb_2PtF_6–Rb_2SiF_6 with excitation at 337.1 nm. Intense emission as a yellow-orange glow is observed in every case even at room temperature. At room temperature only a broad featureless band is observed with the maximum in each case: Cs_2PtF_6, 648.0 ± 3 nm; Cs_2PtF_6–Cs_2SiF_6 and Cs_2PtF_6–Cs_2GeF_6, 620.0 ± 2 nm; and Rb_2PtF_6–Rb_2SiF_6, 600.0 ± 2 nm. At 5 K well-resolved structure appears. The luminescence spectra at 5 K of a pure Cs_2PtF_6 crystal and a mixed Cs_2PtF_6–Cs_2SiF_6 crystal are shown in Figures 1 and 2, respectively.

Emission Lifetime Measurements. These were performed on single crystals of Cs_2PtF_6, Cs_2PtF_6–Cs_2SiF_6, Cs_2PtF_6–

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