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Chemical Applications of Topology and Group Theory. I. Coordination Polyhedra

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Abstract: Possible polyhedra for coordination numbers four through nine, inclusive, are generated by considering 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 $4 \leq v \leq 9$. The polyhedra corresponding to the various possible sp^{3}d^n hybrids are next examined. Polyhedra with minimum flexibilities, maximum symmetries, and maximum numbers of faces are favored in actual complexes.

Recently there has been considerable interest in complexes with unusual coordination numbers and coordination polyhedra. Reviews have appeared on complexes with coordination numbers five,[2] seven,[3] eight,[3,4] and larger.[3] Furthermore the discovery of trigonal-prismatic complexes[5] has demonstrated the possibility for more than one coordination polyhedron even for coordination number six.

Even though a variety of coordination polyhedra are now known, no attempts have yet been made to examine all coordination polyhedra that are possible on a purely mathematical basis. This paper conducts such an examination of coordination polyhedra utilizing several chemically reasonable assumptions to reduce the possibilities to a manageable number. It is then possible to consider the symmetries of the available orbitals of the central metal atom and arrive at conclusions concerning the favored coordination polyhedra for different coordination numbers in different types of complexes. These conclusions agree remarkably well with actual observations. Some aspects of the approach used in this paper resemble recent topological treatments of boranes[6] and polyhedranes.[7]

Definitions

In a discussion of coordination polyhedra, especially the less familiar ones, it is convenient to introduce the following parameters to describe their geometrical features:

d	dimensionality of the polyhedron. For most of the polyhedra discussed in this paper $d = 3$. Examples of coordination "polyhedra" where $d \neq 3$ are the triangle (*e.g.*, BX_3) and the planar square (*e.g.*, $Ni(CN)_4^{2-}$) where $d = 2$.
v	number of vertices of the polyhedron. This will be equal to the coordination number of the central atom.
e	number of edges of the polyhedron
f	number of faces (two-dimensional) of the polyhedron
t	number of triangular faces of the polyhedron
q	number of quadrilateral faces of the polyhedron
j_i	number of vertices of order i. The order of a vertex refers to the number of edges meeting there. This discussion will be concerned mainly with polyhedra with vertices with orders of 3, 4, and 5.
s	number of symmetry elements in the point group describing the polyhedron.
l	valence of lowest valent vertex. For a three-dimensional polyhedron $l \geq 3$.

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(1) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(2) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), 20, 245 (1966).

(3) E. L. Muetterties and C. M. Wright, *ibid.*, 21, 109 (1967).

(4) S. J. Lippard, *Advan. Inorg. Chem.*, 8, 109 (1967).

(5) R. Eisenberg and J. A. Ibers, *J. Am. Chem. Soc.*, 87, 3776 (1965); E. I. Stiefel and H. B.Gray, *ibid.*, 87, 4012 (1965).

(6) R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, 27, 212 (1957); W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., pp 27–78.

(7) H. P. Schultz, *J. Org. Chem.*, 30, 1361 (1965).

Generation of Possible Polyhedra

For any closed convex three-dimensional polyhedron[8] with only triangular and quadrilateral faces, the following relationships involving the parameters listed above must hold.

(1) Euler's Relationship:[9] $e + 2 = v + f$.

(2) Relationship between the Edges and Faces: $2e = 3t + 4q$. This relationship arises from the fact that each edge is shared by exactly two faces. Furthermore each triangular face contributes three such "half-edges" and each quadrilateral face four such "half-edges." Since no face can have fewer edges than a triangle, the inequality $2e \geq 3f$ must hold in all cases.

(3) Relationship between the Edges and Vertices: $\Sigma i j_i = 2e$. This relationship arises from the fact that each edge connects exactly two vertices.

(4) Totality of Vertices: $\Sigma_i j_i = v$. In three-dimensional polyhedra each vertex must have an order of at least three. Therefore the inequality $3v \leq 2e$ must hold in all cases.

(5) Totality of Faces: $t + q = f$. This assumes that the polyhedron has only triangular and quadrilateral faces. Extension to other types is obvious.

In coordination polyhedra compactness is a desirable attribute. A compact polyhedron will maximize the mutual separation of its vertices on the surface of a sphere. Ligand–ligand repulsion will therefore be minimized by maximizing the compactness of the polyhedron. Furthermore, a compact polyhedron will minimize the metal–ligand distances and hence maximize the metal–ligand bond strength. Compactness will be maximized by maximizing the number of edges of a polyhedron. When considering a given coordination number (constant number of vertices), maximizing the number of edges is equivalent to maximizing the number of faces because of Euler's relationship. This means that coordination polyhedra with all triangular faces will be favored in the absence of other factors. For brevity, polyhedra with all triangular faces will be known as "triangulated polyhedra." Such triangulated polyhedra approximate a sphere more closely than non-triangulated polyhedra with the same number of vertices. The commonly encountered polyhedra for coordination numbers four through nine (tetrahedron, trigonal bipyramid, octahedron, pentagonal bipyramid, D_{2d} dodecahedron, and 4,4,4-tricapped trigonal prism, respectively) all have all triangular faces. Polyhedra with quadrilateral faces (*e.g.*, square pyramid, trigonal prism, and square antiprism) are also encountered in coordination chemistry, but polyhedra with pentagonal and/or higher polygonal faces are unknown in coordination chemistry. Polyhedra in this latter category will be excluded from consideration in this treatment for both this empirical reason and because of their lesser compactness as described above.

With these considerations in mind possible coordination polyhedra may be generated by selecting a number of vertices equal to the coordination number of interest and then determining numbers of edges and faces which satisfy Euler's relationship and the inequalities $2e \geq 3f$ and $3v \leq 2e$ discussed above. If polyhedra with only triangular and quadrilateral faces are considered, the numbers of triangular and quadrilateral faces (t and q) and the number of i-valent vertices (j_i) may then be unambiguously determined.

Table I summarizes the coordination polyhedra so determined for coordination numbers four through nine, inclusive. A coordination number of four is selected for the minimum to be considered because four vertices is the minimum number for a three-dimensional polyhedron ($d = 3$). A coordination number of nine is selected as the maximum to be considered since it is the maximum coordination number possible for a metal atom using only s, p, and d orbitals. The polyhedra in Table I can be identified by their values for v, e, and f. Thus a tetrahedron can be designated as the 4,6,4-polyhedron and the octahedron as the 6,12,8-polyhedron. In generating the polyhedra in Table I it is sometimes useful to combine the relationships $e + 2 = v + f$, $2e \geq 3f$, and $3v \leq 2e$ to give the relationships $2v - 4 \geq f \geq v/2 + 2$ and $3v - 6 \geq e \geq 3v/2$. The 9,14,7-polyhedron is omitted from Table I since it cannot be generated without using pentagonal faces.

After finding possible combinations of values for the parameters v, e, f, t, q, and j_i which satisfy the relationships 1 through 5, inclusive, the actual polyhedra of maximum symmetry with these possible combinations of values for the parameters are next found. In the less obvious cases finding the actual polyhedra may be sometimes facilitated by capping a face of a previously determined polyhedron having one less vertex or by dualization of a previous identified polyhedron. Capping a polyhedron P_1 consists of adding a new vertex above the center of one of its faces F_1 followed by adding edges to connect the new vertex with each vertex of F_1. This capping process gives a new polyhedron P_2 with one more vertex than P_1. If a triangular face is capped, the following relationships will be satisfied where the subscripts 1 and 2 refer to P_1 and P_2, respectively: $v_2 = v_1 + 1$; $e_2 = e_1 + 3$; $f_2 = f_1 + 2$. Similarly, if a quadrilateral face is capped, the following relationships will be satisfied: $v_2 = v_1 + 1$; $e_2 = e_1 + 4$; and $f_2 = f_1 + 3$. In the nomenclature of polyhedra used in Table I, a capped face is designated by an Arabic numeral denoting its number of sides. Two polyhedra P_1 and P_2 are dual[10] if the following relationships are satisfied: $v_2 = f_1$; $e_2 = e_1$; $f_2 = v_1$. A given polyhedron, P_1, can be converted to its dual form, P_2, by locating the centers of the faces of P_2 at the vertices of P_1 and the vertices of P_2 above the midpoints of the faces of P_1.

Several "degenerate" polyhedra ($l < 3$) are also encountered. The planar triangle and square are familiar as representing the coordination polyhedra for sp^2 and dsp^2 hybridization, respectively. They satisfy Euler's relationship if they are regarded as having two faces, the "top" and "bottom" faces. Unfamiliar is the degenerate 5,7,4-polyhedron ($l = 2$) which belongs to the C_s point group and has two triangular and two bent quadrilateral faces; in this paper this polyhedron will be called the "twisted wedge." As will be seen below, the twisted wedge appears to occur in certain five-coordinate complexes.

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(8) For a general discussion of the combinatorial and other properties of convex polyhedra and other polytopes, see B. Grünbaum, "Convex Polytopes," Interscience Publishers, New York, N. Y., 1967.

(9) Reference 8, pp 130–138.

(10) Reference 8, pp 46–48.

Table I. Possible Coordination Polyhedra ($v \leq 9, d = 3, l \nless 3$)

Polyhedron	No. of elements[a]			Types of faces[a]		Types of vertices[a]			Point group[b]	Other parameters[a]			
	v	e	f	t	q	j_3	j_4	j_5		s	p	l	x
(A) Coordination no. four													
Tetrahedron	4	6	4	4	0	4	0	0	T_d	24	1	3	1
(B) Coordination no. five													
Square pyramid	5	8	5	4	1	4	1	0	C_{4v}	8	1	3	1
Trigonal bipyramid	5	9	6	6	0	2	3	0	D_{3h}	12	1	3	1
(C) Coordination no. six													
Trigonal prism	6	9	5	2	3	6	0	0	D_{3h}	12	3	3	1
Irregular hexahedron	6	10	6	4	2	4	2	0	C_2	2	7	3	6
Diagonally deficient cube	6	11	7	6	1	2	4	0	C_{2v}	4	2	3	2
Octahedron	6	12	8	8	0	0	6	0	O_h	48	1	4	1
(D) Coordination no. seven													
Tetragonal base–trigonal base	7	11	6	2	4	6	1	0	C_s	2	3	3	3
3-Capped trigonal prism	7	12	7	4	3	4	3	0	C_{3v}	6	4	3	2
4-Capped trigonal prism	7	13	8	6	2	2	5	0	C_{2v}	4	2	3	2
Skewed tetragonal base–trigonal base	7	14	9	8	1	3	1	3	C_s	2	7	3	6
Pentagonal bipyramid	7	15	10	10	0	0	5	2	D_{5h}	20	3	4	1
(E) Coordination no. eight													
Cube	8	12	6	0	6	8	0	0	O_h	48	0	3	0
"Distorted cube"	8	13	7	2	5	6	2	0	C_{2v}	4	3	3	1
Truncated octahedron	8	14	8	4	4	4	4	0	D_{2h}	8	0	3	0
3,3-Bicapped trigonal prism	8	15	9	6	3	2	6	0	D_{3h}	12	0	3	0
Square antiprism	8	16	10	8	2	0	8	0	D_{4d}	16	1	4	1
4,4-Bicapped trigonal prism	8	17	11	10	1	0	6	2	C_{2v}	4	2	4	2
"Dodecahedron"	8	18	12	12	0	0	4	4	D_{2d}	8	1	4	1
(F) Coordination no. nine													
Doubled trigonal prism	9	15	8	2	6	6	3	0	D_{3h}	12	1	3	1
Capped cube	9	16	9	4	5	4	5	0	C_{4v}	8	0	3	0
Square-capped 8,13,7-polyhedron	9	17	10	6	4	2	7	0	C_{2v}	4	0	3	0
Dibasal-bicapped 7,11,6-polyhedron	9	18	11	8	3	1	7	1	C_s	2	1	3	1
3,4,3-Tricapped trigonal prism	9	19	12	10	2	2	3	4	C_{2v}	4	0	3	0
4-Capped square antiprism	9	20	13	12	1	0	5	4	C_{4v}	8	1	4	1
4,4,4-Tricapped trigonal prism	9	21	14	14	0	0	3	6	D_{3h}	12	1	4	1
(G) Some "polyhedra" with $d \neq 3$ and $l = 2$													
Planar triangle ($d = 2$)	3	3	2	2	0	$j_2 = 3, j_{3-5} = 0$			D_{3h}	12	...	2	...
Planar square ($d = 2$)	4	4	2	0	2	$j_2 = 4, j_{3-5} = 0$			D_{4h}	16	...	2	...
"Twisted wedge"	5	7	4	2	2	$j_2 = 1, j_3 = 4, j_{4.5} = 0$			C_s	2	5	2	3

[a] See text for the definitions and symbols. [b] The point group of highest symmetry is given. Distortions can lower the actual symmetry.

Hybridization Schemes

Table I summarizes the topologically possible coordination polyhedra. In order to determine whether these coordination polyhedra can occur in actual complexes, combinations of metal orbitals which form hybrid orbitals directed toward the vertices of these polyhedra must be found. Only s, p, and d orbitals will be considered. Presently available data suggest that f orbitals are involved but rarely in bonding and form relatively weak bonds. This analysis of possible coordination polyhedra in terms of possible hybrid orbitals approximates more closely the situation in strong field complexes such as the carbonyls and cyanides where the major contribution to the strength of the metal–ligand bond comes from the overlap of the metal hybrid orbitals with ligand σ orbitals than the situation in weak field complexes such as hydrates and fluorides where electrostatic forces between the metal atom and the ligand account for a more significant portion of the bond energy. In a search for possible metal orbital hybrids, the assumption will be made that the s and three p orbitals will be used first whenever permitted by symmetry properties, leaving the d orbitals to furnish any additional metal orbitals needed. The only known case where d orbitals are used in the metal σ-bonding hybrid orbitals before all available p orbitals occurs in the square-planar sp^2d system where symmetry properties clearly exclude participation of one of the p orbitals.

The different possibilities for coordination numbers two, three, and four are limited, already well understood, and not particularly interesting. The various possibilities for coordination numbers from five to nine obtained by adding various combinations of the five d orbitals to the sp^3 hybrid are of considerably greater interest. Table II summarizes the 32 ($=2^5$) possible sp^3d^n ($0 \leq n \leq 5$) hybrids utilizing different combinations of the five d orbitals.

The possible geometries for the sp^3d^n hybrid orbitals in Table II were determined by conventional group theoretical methods[11] considering the coordination polyhedra in Table I as well as some distortions of the more symmetrical polyhedra such as the D_{2h} 6,12,8-"rectangular bipyramid" formed by squeezing a regular octahedron as if symmetrically stepping on it and the D_{3d} 6,12,8-trigonal antiprism formed by stretching a regular octahedron by symmetrically pulling on opposite faces. In some cases (*e.g.*, the familiar 6,12,8-octahedron), the hybrid involving s, p, and d orbitals is uniquely determined. In other cases (*e.g.*, the 7,14,9-polyhedron) there are several possible hybrids involving s, p, and d orbitals. In still other cases (*e.g.*, the 8,12,6-cube familiar almost everywhere except coordination chemistry), no hybrid is possible involving just s, p, and

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[11] For a summary of these techniques see F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, New York, N. Y., 1963.

Table II. Coordination Polyhedra Corresponding to Various Possible Combinations of d Orbitals[a]

Coord no.	d orbitals used for σ bonding: xy	yz	zx	$x^2 - y^2$	z^2	Possible polyhedra[b]
4	0	0	0	0	0	4,6,4-Tetrahedron (1)
5	0	0	0	0	1	5,9,6-Trigonal bipyramid (1); 5,7,4-twisted wedge (3)
5	0	0	0	1	0	5,8,5-Tetragonal pyramid (1); 5,7,4-twisted wedge (3)
5	0	0	1	0	0	5,7,4-Twisted wedge (3)
5	0	1	0	0	0	5,7,4-Twisted wedge (3)
5	1	0	0	0	0	5,7,4-Twisted wedge (3)
6	0	0	0	1	1	6,12,8-Octahedron (1)
6	0	0	1	0	1	6,11,7-Diagonally deficient cube (2); 6,10,6-C_2-polyhedron (6)
6	0	1	0	0	1	6,10,6-C_2-Polyhedron (6)
6	1	0	0	0	1	6,12,8-D_{2h}-Rectangular bipyramid (2)
6	0	0	1	1	0	6,11,7-Diagonally deficient cube (2); 6,10,6-C_2-polyhedron (6)
6	0	1	0	1	0	6,10,6-C_2-Polyhedron (6)
6	1	0	0	1	0	6,12,8-D_{2h}-Rectangular bipyramid (2), 6,12,8-D_{3d}-trigonal antiprism (2)
6	0	1	1	0	0	6,9,5-Trigonal prism (1); 6,12,8-D_{3d}-trigonal antiprism (2)[c]
6	1	0	1	0	0	6,9,5-Trigonal prism (1); 6,12,8-D_{3d}-trigonal antiprism (2)[c]
6	1	1	0	0	0	6,9,5-Trigonal prism (1); 6,12,8-D_{3d}-trigonal antiprism (2)[c]
7	1	0	0	1	1	7,15,10-Pentagonal bipyramid (1); 7,12,7-3-capped trigonal prism (2)[d]
7	0	1	0	1	1	7,15,10-Pentagonal bipyramid (1); 7,12,7-3-capped trigonal prism (2)[d]
7	0	0	1	1	1	7,15,10-Pentagonal bipyramid (1); 7,12,7-3-capped trigonal prism (2)[d]
7	1	0	1	0	1	7,13,8-4-Capped trigonal prism (2); 7,14,9-polyhedron (6)
7	1	1	0	0	1	7,14,9-Polyhedron (6)
7	0	1	1	0	1	7,12,7-3-Capped trigonal prism (2); 7,11,6-polyhedron (3)
7	1	0	1	1	0	7,13,8-4-Capped trigonal prism (2); 7,14,9-polyhedron (6)
7	1	1	0	1	0	7,14,9-Polyhedron (6)
7	0	1	1	1	0	7,11,6-Polyhedron (3)
7	1	1	1	0	0	7,11,6-Polyhedron (3)
8	1	1	1	1	0	8,16,10-Square antiprism (1); 8,17,11-4,4-bicapped trigonal prism (2)
8	1	1	1	0	1	8,18,12-D_{2d}-Dodecahedron (1); 8,17,11-4,4-bicapped trigonal prism (2)
8	1	1	0	1	1	8,13,7-C_{2v}-Polyhedron (1)
8	1	0	1	1	1	8,13,7-C_{2v}-Polyhedron (1)
8	0	1	1	1	1	8,13,7-C_{2v}-Polyhedron (1)
9	1	1	1	1	1	9,21,14-4,4,4-Tricapped trigonal prism (1); 9,20,13-, 9,18,11-, and 9,15,8-polyhedra (1)

[a] All of the hybrids listed in this table also utilize the one s and three p orbitals. [b] The flexibility values of the polyhedra are given in parentheses. [c] The 6,10,6-polyhedron can also use this hybridization. [d] The 7,14,9-polyhedron can also use this hybridization.

d orbitals. The number of the 32 possible sp^3d^n combinations which can form a given polyhedral hybrid may be called the permutivity, *p*, of the polyhedron. Thus the 6,12,8-octahedron, 7,14,9-polyhedron, and 8,12,6-cube have permutivity values of 1, 7, and 0, respectively (Table I).

Another property of a polyhedron apparently of more fundamental importance is its flexibility, *x*. The flexibility of a polyhedron is the number of the 32 possible sp^3d^n combinations which can form the polyhedron *in a fixed orientation in space* relative to the axis system. The flexibility of a given polyhedron thus differs from its permutivity in that the permutivity considers all of its spatial orientations whereas the flexibility considers only a specific spatial orientation. For example, some polyhedra such as the 6,9,5-trigonal prism and the 7,15,10-pentagonal bipyramid have unit flexibilities but permutivities of three since the permutivities can consider three different orientations of the polyhedron relative to the Cartesian coordinates. The permutivity relates to the number of times a given polyhedron appears in Table II. The flexibility may relate to the stability of a given polyhedron relative to others of the same coordination number. A higher flexibility of a given polyhedron means a greater probability of rearrangement to another polyhedron corresponding to a similar sp^3d^n hybrid, possibly of lower nonzero flexibility. In all cases the triangulated polyhedron is a minimum nonzero flexibility polyhedron for a given coordination number.

In the absence of special perturbations, the favored polyhedron for a given coordination number is triangulated, thereby maximizing the number of edges and faces and the closeness of the approximation to a sphere. Examples of perturbations which can cause distortion from the triangulated polyhedron include the following.

(1) Unusual and Nonspherical Electronic Configuration of the Metal Atom. The best known example of this phenomenon occurs with the d^8 transition metal systems such as Rh(I), Pd(II), Pt(II), and Au(III) where complexes with coordination number four utilize the planar square rather than the tetrahedron.

(2) Retrodative Bonding Effects. In some cases the need for filled metal orbitals of proper symmetry to engage in retrodative bonding to empty ligand orbitals required for stability of the metal–ligand bond may preempt the metal orbitals which would be required for hybridization to form the triangulated polyhedron. Therefore an alternate hybridization scheme is used which results in a polyhedron with some quadrilateral faces. This may be the factor that causes some hexacoordinate ethylenedithiolate derivatives of the early and middle transition metals of the type $(R_2C_2S_2)_3M$ to assume the trigonal prismatic rather than the octahedral configuration.

(3) Stereochemistry of Ligands. In some cases the shape of the ligand may impose constraints on the coordination polyhedron. Thus metal complexes of phthalocyanines and porphyrins would have to utilize a coordination polyhedron which has all four coordinating nitrogen atoms of the ligand at the corners of a planar square.

The nontriangulated polyhedra arising from perturbations such as those exemplified above may be regarded as arising from the triangulated polyhedron with the same number of vertices by successive edge rupture followed by the distortions necessary to preserve planarity of the newly formed quadrilateral faces. This process is conveniently called "detriangulation." The energy profile of the detriangulation of triangulated polyhedra will have local minima whenever polyhedra with planar faces are reached but will have absolute minima when polyhedra of unusually high symmetry and/or low flexibility are reached. Thus successive detriangulation of a regular 6,12,8-octahedron will lead eventually to the 6,9,5-trigonal prism *via* the intermediate 6,10,6- and 6,11,7-polyhedra.

In the cases of coordination numbers eight and nine involving central metal atoms using only s, p, and d orbitals, some of the nontriangulated polyhedra are inaccessible by detriangulation of the corresponding triangulated polyhedra without passing through a polyhedron which cannot be formed by an sp^{m}d^n hybrid. Such inaccessible polyhedra are not found. The best example of an inaccessible polyhedron occurs in the case of coordination number eight where distortion of the triangulated 8,18,12-dodecahedron to the 8,13,7-polyhedron must involve an intermediate 8,15,9-3,3-bicapped trigonal prism which cannot be formed using only s, p, and d orbitals. The 8,13,7-polyhedron is not found in eight-coordinate complexes even though it is the minimum flexibility polyhedron for sp^{3}d^4[xy,yz,x^2-y^2,z^2] and equivalent hybridizations and even though this hybridization cannot be used to form any of the accessible eight-coordinate polyhedra.

With these general considerations in mind, the coordination polyhedra for coordination numbers five through nine, inclusive, can be considered separately.

(1) Coordination Number Five. The triangulated five-coordinate polyhedron is the D$_{3h}$ trigonal bipyramid of unit flexibility which uses sp^{3}d[z^2] hybridization. This polyhedron is found in the majority of five-coordinate complexes.[2] The C$_{4v}$ 5,8,5-square pyramid also of unit flexibility but using sp^{3}d[x^2-y^2] hybridization is expected to occur in cases where four ligand atoms must be coplanar such as in the phthalocyanine derivatives with one additional ligand. In other cases coplanarity of four ligands is not an absolute necessity but is favored in order to maximize delocalization. This is the case with five-coordinate complexes with two chelate organosulfur ligands such as ethylenedithiolate or dialkyldithiocarbamate derivatives. The square-pyramidal configuration is thus predicted for such complexes and has been found experimentally for complexes such as (R$_2$NCS$_2$)$_2$CoNO.[12] The remaining three possible five-coordinate hybridizations fit neither the D$_{3h}$ trigonal bipyramid nor the C$_{4v}$ square pyramid but can be accommodated by the 5,7,4-twisted wedge, a polyhedron with two nonplanar quadrilateral faces. The observed stereochemistry[13] for the 2,2′,2′′-terpyridyl complex (terpy)ZnCl$_2$ represents a distortion from the trigonal bipyramid which closely approximates the twisted wedge.

(2) Coordination Number Six. The very symmetrical and triangulated O$_h$ octahedron with sp^{3}d^2[x^2-y^2,z^2] hybridization and unit flexibility is overwhelmingly favored for this coordination number. The D$_{3h}$ 6,9,5-trigonal prism with sp^{3}d^2[xy,zy] or equivalent hybridization and also unit flexibility is found for tris(ethylenedithiolate) derivatives of early and middle transition metals[5] such as (R$_2$C$_2$S$_2$)$_3$Re where additional π bonding involving the carbon–carbon double bonds and/or the sulfur atoms of the ethylenedithiolate ligands may be responsible for the deviation from the octahedron. The lower symmetry C$_2$ 6,10,6-polyhedron (flexibility 6) is found in the maleonitrile dithiolate derivative [(CH$_3$)$_4$N]$_2$[V(S$_2$C$_2$(CN$_2$)$_2$)$_3$].[14] The following three polyhedra are minimum flexibility polyhedra for other sp^{3}d^2 hybrid combinations which have not yet been found in actual complexes.

(a) C$_{2v}$ 6,11,7-Polyhedron. This polyhedron may be conveniently designated as the "diagonally deficient cube," since it is formed by removal from a cube of two vertices located at the ends of a diagonal of one of the faces. It is most likely to be found in a six-coordinate complex with four coordination positions occupied by a planar tetradentate ligand such as the porphyrins or phthalocyanines and the two remaining coordination positions occupied by a bidentate chelating ligand of relatively small "bite."

(b) D$_{2h}$ 6,12,8-Rectangular Bipyramid. This polyhedron may be obtained by squeezing the octahedron. Its "axes" have symmetry properties similar to those of the monoclinic crystal system. It is the minimum flexibility polyhedron for the hybridization sp^{3}d^2[xy,z^2] and also corresponds to the hybridization sp^{3}d^2[xy,x^2-y^2]. It is most likely to be found in a six-coordinate complex with two monodentate ligands and two bidentate ligands with a small "bite" and with electronic effects making the four coordinating atoms of the two bidentate ligands coplanar.

(c) C$_{5v}$ 6,10,6-Pentagonal Pyramid. This polyhedron has unit flexibility corresponding to the hybridization sp^{3}d^2[xy,x^2-y^2]. The treatment in this paper excluded this polyhedron from consideration because of its pentagonal face. No unambiguous examples of this polyhedron are known. Xenon hexafluoride has a nonoctahedral but otherwise unknown structure;[15] a pentagonal pyramidal arrangement for the six fluorines in xenon hexafluoride is a distinct possibility arising from the seven-coordinate D$_{5h}$ pentagonal bipyramid with a lone pair in one of the apical positions.

(3) Coordination Number Seven. Decisions between the various possible coordination polyhedra for seven-coordinate complexes are more difficult than for higher or lower coordination numbers for the following reasons: (a) more polyhedra are possible for the coordination number seven than for lower coordination numbers; (b) no seven-coordination polyhedra can be excluded as being impossible to form by sp^{m}d^n hybridization as is the case with some of the polyhedra for coordination numbers eight and nine; (c) since seven is a prime number, fewer polyhedra of obviously high symmetry are found.

The triangulated seven-coordinate polyhedron of maximum symmetry is the D$_{5h}$ 7,15,10-pentagonal bipyramid of unit flexibility corresponding to sp^{3}d^3[xy,x^2-y^2,z^2] and equivalent hybridizations. This polyhedron is encountered in numerous seven-coor-

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(12) P. R. H. Aldeman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

(13) D. E. C. Corbridge and E. G. Cox, *ibid.*, 594 (1956).

(14) E. I. Stiefel, Z. Dori, and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3353 (1967).

(15) L. S. Bartell, R. M. Gavin, Jr., and H. B. Thompson, *J. Chem. Phys.*, 43, 2547 (1965).

dinate derivatives such as iodine heptafluoride,[16] IF_7. A triangulated seven-coordinate polyhedron of lower (C_{3v}) symmetry than the pentagonal bipyramid is the 7,15,10-3-capped octahedron of flexibility two corresponding to the $sp^3d^3[xy,x^2-y^2,z^2]$, $sp^3d^3[yz,zx,z^2]$, and equivalent hybridizations. This polyhedron has been suggested[17] for certain seven-coordinate niobium and tantalum complexes.

Several nontriangulated seven-coordinate polyhedra are possible. The C_{2v} 7,13,8-4-capped trigonal prism is the minimum flexibility ($x = 2$) polyhedron for the hybridizations $sp^3d^3[xy,zx,z^2]$ and $sp^3d^3[xy,zx,x^2-y^2]$; this polyhedron is encountered in certain seven-coordinate derivatives such as the heptafluoroniobate,[18] NbF_7^{2-}. The relatively unsymmetrical (C_s) 7,14,9-polyhedron with one tetragonal base and one trigonal base is the most nearly triangulated minimum flexibility ($x = 6$) polyhedron for the $sp^3d^3[xy,yz,z^2]$ and $sp^3d^3[xy,yz,x^2-y^2]$ hybridizations; this polyhedron is found in the monoclinic forms of ZrO_2 and HfO_2.[19] No unambiguous examples of the less triangulated 7,12,7-3-capped trigonal prism and 7,11,6-polyhedron are known in coordination chemistry.

(4) Coordination Number Eight. The triangulated eight-coordinate polyhedron is the D_{2d} 8,18,12-dodecahedron of unit flexibility corresponding to $sp^3d^4[xy,yz,zx,z^2]$ hybridization. Numerous eight-coordinate complexes[3,4] utilize this polyhedron. Detriangulation of the 8,18,12-dodecahedron proceeds *via* the 8,17,11-4,4-bicapped trigonal prism (flexibility 2) to give the D_{4d} 8,16,10-square antiprism of unit flexibility corresponding to the $sp^3d^4[xy,yz,zx,x^2-y^2]$ hybridization. Numerous eight-coordinate complexes utilize the square antiprism. The intermediate C_{2v} 8,17,11-4,4-bicapped trigonal prism is also found in some lanthanide trihalides.[20] Further detriangulation of the square antiprism is blocked by the zero permutivity of the next stage, the D_{3h} 8,15,9-3,3-bicapped trigonal prism. For this reason $sp^3d^4[xy,yz,x^2-y^2,z^2]$ and equivalent hybridizations which correspond only to the C_{2v} 8,13,7-polyhedron are inaccessible by detriangulation of the triangulated eight-coordinate polyhedron. The detriangulation of the favored D_{2d} 8,18,12-dodecahedron of unit flexibility through the less favored C_{2v} 8,17,11-4,4-bicapped trigonal prism to the more favored D_{4d} 8,16,10-square antiprism with a zero permutivity barrier to further detriangulation provides an energy profile for the eight-coordinate polyhedra similar to that given by Muetterties and Wright[21] if the portion of their energy curve corresponding to higher energy polyhedra requiring f orbitals is ignored.

(5) Coordination Number Nine. The triangulated nine-coordinate polyhedron of maximum symmetry is the D_{3h} 9,21,14-4,4,4-tricapped trigonal prism and corresponds to the single possible sp^3d^5 hybrid (*i.e.*, $x = 1$). The relatively few known nine-coordinate complexes including the unusual hydrides[22] ReH_9^{2-} and TcH_9^{2-} utilize this polyhedron. Detriangulation of the tricapped trigonal prism can occur to give the C_{4v} 9,20,13-4-capped square antiprism, but further detriangulation is blocked by the zero permutivity C_{2v} 9,19,12-3,4,3-tricapped trigonal prism.

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(16) R. E. Lavilla and S. H. Bauer, *J. Chem. Phys.*, 33, 182 (1960).

(17) J. L. Hoard and W. J. Martin, *J. Am. Chem. Soc.*, 63, 11 (1941); M. B. Williams and J. L. Hoard, *ibid.*, 64, 1139 (1942).

(18) G. M. Brown and L. A. Walker, *Acta Cryst.*, 20, 220 (1966).

(19) J. D. McCullough and K. N. Trueblood, *ibid.*, 12, 507 (1959); D. K. Smith and H. W. Newkirk, *ibid.*, **18**, 983 (1965); J. Adam and M. D. Rogers, *ibid.*, 12, 951 (1959).

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

(21) Reference 3, Figure 24.

(22) K. Knox and A. P. Ginsberg, *Inorg. Chem.*, 3, 555 (1964); S. C. Abrahams, A. P. Ginsberg, and K. Knox, *ibid.*, 3, 559 (1964).