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Atomic orbitals, symmetry, and coordination polyhedra

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This paper is dedicated to Professor Ronald J. Gillespie in recognition of his pioneering work in understanding the shape of molecules.

Contents

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Abstract

The fundamental ideas on inorganic stereochemistry presented originally by Sidgwick and Powell in 1940 and developed subsequently by Gillespie and Nyholm in 1957 have expanded into a broad theoretical base for essentially all of coordination chemistry during the subsequent four decades. A key aspect of this work has been a detailed understanding of the topology, shape, and symmetry of all of the actual and plausible polyhedra found in coordination chemistry and the relationship of such properties of the relevant polyhedra to those of the available atomic orbitals of the central metal atom. This paper reviews the polyhedra for coordination numbers four through nine for the spherical nine-orbital sp^3d^5 manifold commonly used in transition metal coordination chemistry as well as possibilities in coordination complexes having other spherical manifolds for the central atom including the four-orbital sp^3 manifold used by elements without energetically accessible d orbitals, the six-orbital sd^5 manifold used in some early transition metal alkyls and hydrides, and the thirteen-orbital sd^5f^7 manifold used in actinide complexes.

Keywords: Atomic orbitals; Symmetry; Coordination polyhedra

1. Introduction

One of the important objectives of theoretical chemistry is understanding the factors affecting the shapes of molecules. In the specific area of coordination chemistry this often corresponds to understanding the coordination polyhedra favored for particular metals, oxidation states, and ligand sets. In this connection a seminal paper was the 1940 Bakerian Lecture of Sidgwick and Powell [1] on stereochemical types and valency groups. This paper was the first to develop the idea of the relation between the number of valence electrons, number of ligands, and the shape of the molecule and led to the so-called Sidgwick–Powell theory of electron pair repulsions. By the 1940 publication date of this paper, enough experimental structural data had been accumulated on key coordination compounds and other inorganic molecules using X-ray diffraction as well as absorption spectra and Raman spectra so that an adequate experimental data base throughout the periodic table had become available to test these ideas.

The next key paper in this area was a review on inorganic stereochemistry by Gillespie and Nyholm [2] which introduced the idea that the pairs of electrons in a valency shell, irrespective of whether they are shared (i.e., bonding) pairs or unshared (i.e., non-bonding) pairs, are always arranged in the same way which depends only on their number. Thus two pairs are arranged linearly, three pairs in the form of a plane triangle, four pairs tetrahedrally, five pairs in the form of a trigonal bipyramid, six pairs octahedrally, etc. These ideas were subsequently developed in more detail in a 1972 book by Gillespie [3] and led to the so-called *valence-shell electron pair repulsion* (VSEPR) theory. This theory has proven particularly useful over the years in understanding the shapes of hypervalent main group element molecules such as SF_4, ClF_3, etc.

During the period that these theoretical ideas were developing, additional experimental information also accumulated, aided by the growing availability of X-ray diffraction methods to elucidate unambiguously the structures of diverse inorganic and organometallic compounds. In the late 1960s, I became interested in exploring the extent to which elementary concepts from the mathematical discipline of topology could account for the specific coordination polyhedra that were being discovered in inorganic compounds and I summarized my initial observations in a 1969 paper [4]. In the three decades since publication of this original paper I have introduced a number of additional ideas relating to coordination polyhedra, so that the approach of the original 1969 paper now appears very crude. Ideas which have proven to be useful over the years include the concept of coordination polyhedra which are symmetry-forbidden for a given atomic orbital manifold [5] as well as the relationship of the magnetic quantum number of the atomic orbitals involved in the hybridization to the shape of the resulting coordination polyhedron [6]. This paper summarizes the interplay between these ideas and how they relate to the experimentally observed shapes of coordination compounds.

2. Properties of atomic orbitals

2.1. Atomic orbitals from spherical harmonics

The shapes of the atomic orbitals of the central atom determine the stereochemistry of the bonding of the central atom to its surrounding ligands, which is based on the hybrid orbitals formed by various linear combinations of the available atomic orbitals. These atomic orbitals arise from the one-particle wave functions Ψ, obtained as spherical harmonics by solution of the following second order differential equation in which the potential energy V is spherically symmetric:

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\Psi=\nabla^2\Psi+\frac{8\pi^2 m}{h^2}(E-V)\Psi=0 \qquad (1)$$

These spherical harmonics Ψ are functions of either the three spatial coordinates x, y, and z or the corresponding spherical polar coordinates r, θ, and ϕ defined by the equations

$$x=r\sin\theta\cos\phi \qquad (2a)$$

$$y=r\sin\theta\sin\phi \qquad (2b)$$

$$z=r\cos\theta \qquad (2c)$$

Furthermore, a set of linearly independent wave functions can be found such that Ψ can be factored into the following product:

$$\Psi(r,\theta,\phi)=\mathrm{R}(r)\cdot\Theta(\theta)\cdot\Phi(\phi) \qquad (3)$$

in which the factors R, Θ, and Φ are functions solely of r, θ, and ϕ, respectively. Since the value of the radial component $\mathrm{R}(r)$ of Ψ is completely independent of the angular coordinates θ and ϕ, it is independent of direction (i.e., *isotropic*) and therefore remains unaltered by any symmetry operations. For this reason all of the symmetry properties of a spherical harmonic Ψ, and thus of the corresponding wave function or atomic orbital, are contained in its angular component $\Theta(\theta)\cdot\Phi(\phi)$. Furthermore, each of the three factors of Ψ (Eq. (3)) generates a quantum number. Thus the factors $R(r)$, $\Theta(\theta)$, and $\Phi(\phi)$ generate the quantum numbers n, l, and m_l (or simply m), respectively. The *principal quantum number n*, derived from the radial component $R(r)$, relates to the distance from the center of the sphere (i.e., the nucleus in the case of atomic orbitals). The *azimuthal quantum number l*, derived from the factor $\Theta(\theta)$ in Eq. (3), relates to the number of nodes in the angular component $\Theta(\theta)\cdot\Phi(\phi)$, where a *node* is a plane corresponding to a zero value of $\Theta(\theta)\cdot\Phi(\phi)$ or Ψ, i.e., where the sign of $\Theta(\theta)\cdot\Phi(\phi)$ changes from positive to negative. Atomic orbitals for which $l = 0, 1, 2$, and 3 have 0, 1, 2, and 3 nodes, respectively, and are conventionally designated as s, p, d, and f orbitals, respectively. For a given value of the azimuthal quantum number l, the *magnetic quantum number* m_l or m, derived from the factor $\Phi(\phi)$ in Eq. (3), may take on all $2l + 1$ different values from $+l$ to $-l$. There are therefore necessarily $2l + 1$ distinct orthogonal orbitals for a given value of l corresponding to 1, 3, 5, and 7 distinct s, p, d, and f orbitals, respectively.

The magnetic quantum number, m, can be related to the distribution of the electron density of the atomic orbital relative to the z axis. Thus if the nucleus is in the center of a sphere in which the z axis is the polar axis passing through the north and south poles, an atomic orbital with $m = 0$ has its electron density oriented towards the north and south poles of the sphere whereas an atomic orbital with the maximum possible value of $|m|$, i.e., $\pm l$, has its maximum electron density in the equator of the sphere. In this way the angular momentum of the atomic orbitals involved in the hybridization for a given coordination polyhedron can relate to the moment of inertia of that coordination polyhedron.

A convenient way of depicting the shape of an orbital, particularly complicated orbitals with large numbers of lobes, is by the use of an orbital graph [7]. In such an orbital graph the vertices correspond to the lobes of the atomic orbitals and the edges to nodes between adjacent lobes of opposite sign. Such an orbital graph is necessarily a bipartite graph in which each vertex is labeled with the sign of the corresponding lobe and only vertices of opposite sign can be connected by an edge.

Table 1 illustrates some of the important properties of s, p, and d orbitals. Similarly Table 2 lists some of the important properties of two different sets of seven f orbitals. The cubic set of f orbitals is used for structures of sufficiently high symmetry (e.g., O_h and I_h) to have sets of triply degenerate f orbitals whereas the general set of f orbitals are used for structures of lower symmetry without sets of f orbitals having degeneracies 3 or higher. The g and h orbitals are analogously depicted elsewhere [8]; they are not relevant to the discussion of coordination polyhedra in this paper.

The conventionally used set of five orthogonal d orbitals contains two types of orbitals, namely the xy, xz, yz, and x^2–y^2 orbitals each with four major lobes and the z^2 orbital with only two major lobes (Table 1). All possible shapes of d orbitals can be expressed as linear combinations of these two types of d orbitals by the following equation [9,10]:

$$\mathrm{d} = a\phi_{z^2} + (1-a^2)^{1/2}\phi_{x^2-y^2} \qquad \frac{\sqrt{3}}{2} = 0.866025 \leq a \leq 1 \tag{4}$$

In Eq. (4), ϕ_{z^2} refers to the wave function of the d_{z^2} atomic orbital and $\phi_{x^2-y^2}$ refers to the function of the $\mathrm{d}_{x^2-y^2}$ atomic orbital, taken as a representative of one of the four d orbitals with four major lobes. Two different sets of five orthogonal *equivalent* d orbitals can be constructed by choosing five orthogonal linear combinations of the d_{z^2} and $\mathrm{d}_{x^2-y^2}$ orbitals using Eq. (4) [9,10] These are called the *oblate* and *prolate* sets of five equivalent d orbitals since they are oriented towards the vertices of an oblate and prolate pentagonal antiprism, respectively. The five-fold symmetry of these equivalent sets of five d orbitals makes them inconvenient to use since relatively few molecules have the matching five-fold symmetry.

2.2. Valence manifolds of atomic orbitals

Valence manifolds of atomic orbitals are the sets of atomic orbitals having suitable energies to participate in chemical bonding. The geometry of such valence manifolds of atomic orbitals relates to contours of the sum $\Sigma\ \psi^2$ over all orbitals in the manifold. Spherical atomic orbital manifolds are valence manifolds of atomic orbitals containing entire sets of atomic orbitals having a given value of the azimuthal quantum number, l, and are isotropic, i.e., they extend equally in all

Table 1
Properties of s, p, and d atomic orbitals

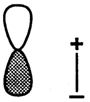
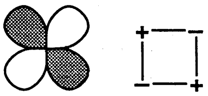
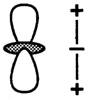
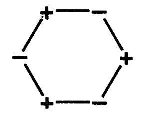
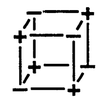
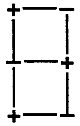
Type	$\lvert m\rvert$	Nodes	Polynomial	Angular function	Appearance and orbital graph	Shape
s	0	0		Independent of θ, ϕ	Spherically symmetrical	Point
p	1	1	x	$\sin\theta\cos\phi$		Linear
p	1	1	y	$\sin\theta\sin\phi$		
p	0	1	z	$\cos\theta$		
d	2	2	xy	$\sin^2\theta\sin 2\phi$		Square
d	2	2	x^2-y^2	$\sin^2\theta\cos 2\phi$		
d	1	2	xz	$\sin\theta\cos\theta\cos\phi$		
d	1	2	yz	$\sin\theta\cos\theta\sin\phi$		
d	0	2	$2z^2-r^2$ (abbreviated as z^2)	$(3\cos^2\theta-1)$		Linear

Table 2
Properties of the f atomic orbitals

$\|m\|$	Lobes	Shape	Orbital graph	General set	Cubic set
3	6	Hexagon		$x(x^2-3y^2)$ $y(3x^2-y^2)$	none
2	8	Cube		xyz $z(x^2-y^2)$	xyz $x(z^2-y^2)$, $y(z^2-x^2)$, $z(x^2-y^2)$
1	6	Double square		$x(5z^2-r^2)$ $y(5z^2-r^2)$	none
0	4	Linear		$z(5z^2-r^2)$	x^3 y^3 z^3

directions similar to a sphere. The following spherical atomic orbital manifolds (Table 3) are of chemical interest [11]:

1. The four-orbital sp^3 manifold ($l=0$ and 1) involved in the chemistry of main group elements including their hypervalent compounds through three-center four-electron bonding;
2. The six-orbital sd^5 manifold ($l=0$ and 2) involved in the chemistry of early transition metal hydrides and alkyls since the p orbitals in such systems may have energies too high to participate in chemical bonding;
3. The nine-orbital sp^3d^5 manifold ($l=0$, 1, and 2) involved in most of the chemistry of the *d*-block transition metals;
4. The 13-orbital sd^5f^7 manifold ($l=0$, 2, and 3) involved in the chemistry of the actinides.

These spherical atomic orbital manifolds are characterized by two numbers (Table 3):

1. The total number of atomic orbitals in the manifold designated as x which corresponds to the maximum possible coordination number using only two-electron two-center bonding;

Table 3
Spherical atomic orbital manifolds

Manifold	Elements involved	Maximum coordination number (x)[a]	Maximum coordination number with an inversion center (y)[a]
sp^3	Main group	4	2
sd^5	Early transition metals	6	0
sp^3d^5	Transition metals	9	6
sd^5f^7	Actinides	13	12

[a] Considers only two-center two-electron metal–ligand bonding.

2. The maximum number of atomic orbitals in a submanifold consisting of equal numbers of gerade and ungerade orbitals designated as y which corresponds to the maximum possible coordination number for a polyhedron with a center of symmetry or a unique reflection plane containing no vertices. For a given manifold, such polyhedra with v vertices where $y < v \leq x$ are symmetry forbidden coordination polyhedra.

A specific feature of the chemical bonding in some systems containing the late transition and early post-transition metals observed by Nyholm [12] as early as 1961 is the shifting of one or two of the outer p orbitals to such high energies that they no longer participate in the chemical bonding and the accessible spd valence orbital manifold is no longer spherical (isotropic). If one p orbital is so shifted to become antibonding, then the accessible spd orbital manifold contains only eight orbitals (sp^2d^5) and has the geometry of a torus or doughnut (Fig. 1(a)). The 'missing' p orbital is responsible for the hole in the doughnut. This toroidal sp^2d^5 manifold can bond only in the two dimensions of the plane of the ring of the torus thereby leading only to planar coordination arrangements. Filling this sp^2d^5 manifold of eight orbitals with electrons leads to the 16-electron configuration found in

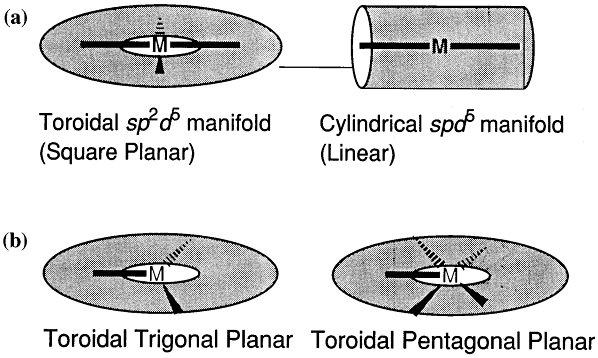


Fig. 1. (a) The toroidal (sp^2d^5) and cylindrical (spd^5) manifolds; (b) Trigonal planar and pentagonal planar coordination for the toroidal manifold.

square planar complexes of the d^8 transition metals such as Rh(I), Ir(I), Ni(II), Pd(II), Pt(II), and Au(III). The locations of the four ligands in these square planar complexes can be considered to be points on the surface of the torus corresponding to the sp^2d^5 manifold. The toroidal sp^2d^5 manifold can also lead to trigonal planar and pentagonal planar coordination for three- and five-coordinate complexes, respectively (Fig. 1(b)). The x, y, and z axes for a toroidal sp^2d^5 manifold are conventionally chosen so that the missing p orbital is the p_z orbital.

In some structures containing the late transition and post-transition metals, particularly the 5*d* metals Pt, Au, Hg, and Tl, two of the outer p orbitals are raised to antibonding energy levels. This leaves only one p orbital in the accessible spd orbital manifold, which now contains seven orbitals (spd^5) and has cylindrical geometry extending in one axial dimension much further than in the remaining two dimensions (Fig. 1(a)). Filling this seven-orbital spd^5 manifold with electrons leads to the 14-electron configuration found in two-coordinate linear complexes of d^{10} metals such as Pt(0), Cu(I), Ag(I), Au(I), Hg(II), and Tl(III). The raising of one or particularly two outer p orbitals to antibonding levels has been attributed to relativistic effects.

The p orbitals which are raised to antibonding levels as noted above can participate in $d\sigma \rightarrow p\sigma^*$ or $d\pi \rightarrow p\pi^*$ bonding in complexes of metals with toroidal sp^2d^5 and cylindrical spd^5 manifolds depending on the symmetry of the overlap (Fig. 2). Such bonding was suggested by Dedieu and Hoffmann [13] in 1978 for Pt(0)–Pt(0) dimers on the basis of extended Hückel calculations and is discussed in detail in a recent review by Pyykkö [14]. This type of surface bonding like, for example, the $d\pi \rightarrow p\pi^*$ backbonding in metal carbonyls, does not affect the electron bookkeeping in the late transition and post-transition metal clusters but accounts for the bonding rather than non-bonding distances between adjacent metal vertices in certain compounds of the coinage metals, particularly gold, as well as other late and post-transition metals.

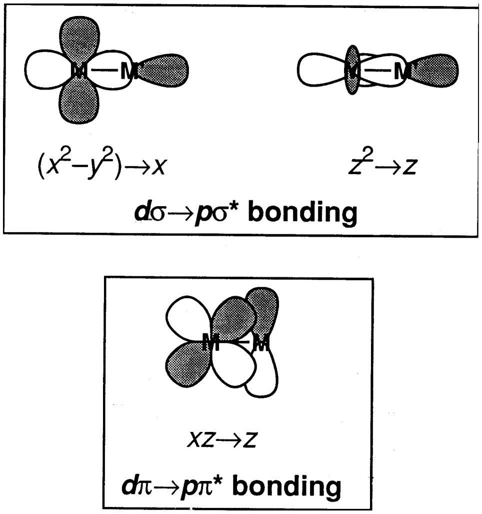


Fig. 2. Examples of $d\sigma \rightarrow p\sigma$ and $d\pi \rightarrow p\pi$ bonding to the otherwise empty p orbitals in complexes of metals with toroidal (sp^2d^5) and cylindrical (spd^5) manifolds.

2.3. Hybridization of atomic orbitals

Consider a metal complex of the general type ML_n in which M is the central metal atom, L_n refers to n ligands surrounding M, and each ligand L is attached to M through a single atom of L. The combined strengths of the n chemical bonds formed by M to the n ligands L are maximized if the metal valence atomic orbitals overlap to the maximum extent with the atomic orbitals of the ligands L. The available metal valence orbitals may be combined or *hybridized* in such a way to maximize this overlap.

Consider a 'light' element of the first row of eight of the periodic table Li → F such as, for example, boron or carbon. The valence orbital manifold of such elements consists of a single s orbital and the three p orbitals, namely p_x, p_y, and p_z. In the example of methane, CH_4, the four hydrogen atoms are located at the vertices of a regular tetrahedron surrounding the central carbon atom. The strengths of the four C–H bonds directed towards the vertices of a regular tetrahedron can be maximized if the following linear combinations of the wave functions of the atomic orbitals in the sp^3 manifold are used:

$$\Psi_1 = \frac{1}{2}\phi_s + \frac{1}{2}\phi_x + \frac{1}{2}\phi_y + \frac{1}{2}\phi_z \tag{5a}$$

$$\Psi_2 = \frac{1}{2}\phi_s - \frac{1}{2}\phi_x - \frac{1}{2}\phi_y + \frac{1}{2}\phi_z \tag{5b}$$

$$\Psi_3 = \frac{1}{2}\phi_s + \frac{1}{2}\phi_x - \frac{1}{2}\phi_y - \frac{1}{2}\phi_z \tag{5c}$$

$$\Psi_4 = \frac{1}{2}\phi_s - \frac{1}{2}\phi_x + \frac{1}{2}\phi_y - \frac{1}{2}\phi_z \tag{5d}$$

In Eqs. (5a)–(5d) the p_x, p_y, and p_z orbitals are abbreviated as x, y, and z, respectively, and the hybrid wave functions are represented by ψ and the component atomic orbitals are represented by ϕ.

The process of determining the coefficients in equations such as those above is beyond the scope of this article and can become complicated when the degrees of freedom are increased by lowering the symmetry of the coordination polyhedron or by increasing the size of the valence orbital manifold to include d orbitals, as is of interest for the transition metal chemistry discussed in this article. However, elementary symmetry considerations, as outlined in group-theory texts [15], can be used to determine which atomic orbitals have the necessary symmetry properties to form a hybrid corresponding to a given coordination polyhedron. For example, the four atomic orbitals of an sp^3 manifold can form four hybrid orbitals pointing towards the vertices of a tetrahedron as outlined above. However, the four atomic orbitals of an sp^3 manifold are excluded by symmetry considerations from forming four hybrid orbitals pointing towards the vertices of a planar square or rectangle. Thus if the plane of the square or rectangle is the xy plane, the p_z orbital is seen to have no electron density in this plane (i.e., the xy plane is a node for the p_z orbital) and thus cannot participate in the bonding to atoms in the plane. In the case of coordination polyhedra with larger numbers of vertices, particularly those of relatively high symmetry such as the cube and hexagonal bipyramid for eight-coordination, the inability of certain combinations of atomic orbitals to form the required hybrid orbitals is not as obvious and more sophisticated group-theoretical methods are required. Such methods are discussed in Section 3.3.

3. The properties of coordination polyhedra

3.1. Topology of coordination polyhedra

A key aspect of the topology of coordination polyhedra is Euler's relationship between the numbers of vertices (v), edges (e), and faces (f), i.e.,

$$v - e + f = 2 \tag{6}$$

This arises from the properties of ordinary three-dimensional space.

In addition the following relationships must be satisfied by any polyhedron:

(1) Relationship between the edges and faces: $\sum_{i=3}^{v-1} if_i = 2e$ (7)

In Eq. (7), f_i is the number of faces with i edges (i.e., f_3 is the number of triangular faces, f_4 is the number of quadrilateral faces, etc.). This relationship arises from the fact that each edge of the polyhedron is shared by exactly two faces. Since no face can have fewer edges than the three of a triangle, the following inequality must hold in all cases:

$$3f \leq 2e \tag{8}$$

(2) Relationship between the edges and vertices: $\sum_{i=3}^{v-1} iv_i = 2e$ (9)

In Eq. (9), v_i is the number of vertices of *degree i* (i.e., having *i* edges meeting at the vertex). This relationship arises from the fact that each edge of the polyhedron connects exactly two vertices. Since no vertex of a polyhedron can have a degree less than three, the following inequality must hold in all cases:

$$3v \leq 2e \tag{10}$$

(3) Totality of faces: $\sum_{i=3}^{v-1} f_i = f$ (11)

(4) Totality of vertices: $\sum_{i=3}^{v-1} v_i = v$ (12)

Eq. (11) relates the f_is to f and Eq. (12) relates the v_is to v.

In generating actual polyhedra, the operations of capping and dualization are often important. *Capping* a polyhedron $\mathscr{P}_1$ consists of adding a new vertex above

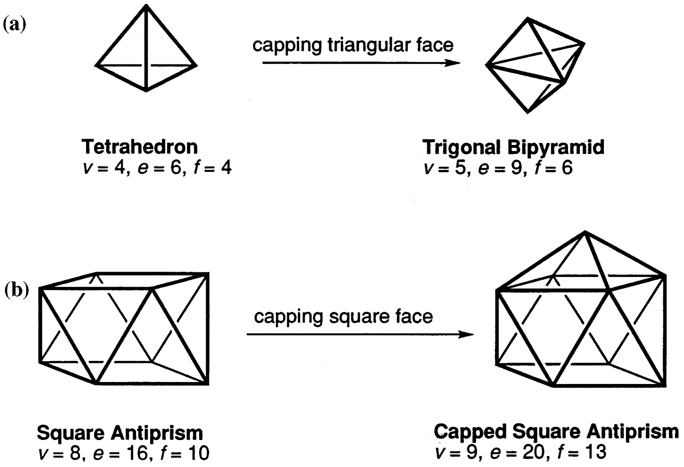


Fig. 3. (a) Capping of a triangular face of a tetrahedron to give a trigonal bipyramid; (b) capping of a square face of a square antiprism to give a capped square antiprism.

the center of one of its faces $\mathscr{F}_1$ followed by adding edges to connect the new vertex with each vertex of $\mathscr{F}_1$. This capping process gives a new polyhedron $\mathscr{P}_2$ having one more vertex than $\mathscr{P}_1$. If a triangular face is capped, the following relationships will be satisfied in which the subscripts 1 and 2 refer to $\mathscr{P}_1$ and $\mathscr{P}_2$, respectively:

$$v_2 = v_1 + 1;\ e_2 = e_1 + 3;\ f_2 = f_1 + 2 \tag{13}$$

Such a capping of a triangular face is found in the capping of a tetrahedron to form a trigonal bipyramid (Fig. 3(a)). In general, if a face with k edges is capped, the following relationships will be satisfied:

$$v_2 = v_1 + 1;\ e_2 = e_1 + k;\ f_2 = f_1 + k - 1 \tag{14}$$

An example of such a capping process converts a square antiprism into a capped square antiprism (Fig. 3(b)).

Another process of interest in polyhedral topology is the *dualization* of polyhedra. A given polyhedron $\mathscr{P}$ can be converted into its dual $\mathscr{P}^*$ by locating the centers of the faces of $\mathscr{P}^*$ at the vertices of $\mathscr{P}$ and the vertices of $\mathscr{P}^*$ above the centers of the faces of $\mathscr{P}$. Two vertices in the dual $\mathscr{P}^*$ are connected by an edge when the corresponding faces in $\mathscr{P}$ share an edge. An example of the process of dualization is the conversion of trigonal bipyramid into a trigonal prism or an octahedron into a cube (Fig. 4). The process of dualization has the following properties:

1. The numbers of vertices and edges in a pair of dual polyhedra $\mathscr{P}$ and $\mathscr{P}^*$ satisfy the relationships $v^* = f$, $e^* = e$, $f^* = v$, in which the starred variables refer to the dual polyhedron $\mathscr{P}^*$. Thus in the case of the trigonal bipyramid ($\mathscr{P}$)/trigonal prism($\mathscr{P}^*$) dual pair (Fig. 4(a)) $v^* = f = 6$, $e^* = e = 9$, $f^* = v = 5$.
2. Dual polyhedra have the same symmetry elements and thus belong to the same symmetry point group. For example, above both the trigonal bipyramid and the

trigonal prism have the D_{3h} symmetry point group (Fig. 4(a)) and both the octahedron and the cube have the O_h symmetry point group (Fig. 4(b)).

3. Dualization of the dual of the polyhedron leads to the original polyhedron.
4. The degrees of the vertices of a polyhedron correspond to the number of edges in the corresponding face polygons in its dual.

The problem of the classification and enumeration of polyhedra is a complicated one. Thus there appear to be no formulas, direct or recursive, for which the number of combinatorially distinct polyhedra having a given number of vertices, edges, faces, or any given combination of these elements can be calculated [16,17]. Duijvestijn and Federico have enumerated by computer the polyhedra having up to 22 edges according to the numbers of vertices, edges, and faces and their symmetry groups and present a summary of their methods, results, and literature references to previous work [18]. Their work shows that there are 1, 2, 7, 34, 257, 2606, and 32,300 topologically distinct polyhedra having 4, 5, 6, 7, 8, 9, and 10 faces or vertices, respectively. Tabulations are available for all $301(=1+2+7+34+257)$ topologically distinct polyhedra having eight or fewer faces [19] or eight or fewer vertices [20]. These two tabulations are essentially equivalent by the dualization relationship discussed above.

3.2. The shapes of coordination polyhedra

The shape of a coordination polyhedron can be defined by its moments of inertia and the shape of the corresponding momental ellipsoid (Fig. 5, [21]). Thus, consider a rigidly oriented collection of n particles such as a set of n ligands located at the vertices of a coordination polyhedron. The moment of inertia of this collection of particles about any axis passing through its center of mass is defined as

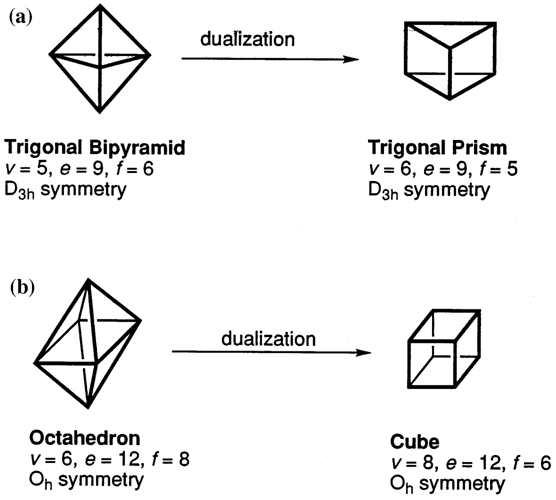


Fig. 4. (a) Dualization of a trigonal bipyramid to give a trigonal prism; (b) dualization of an octahedron to give a cube.

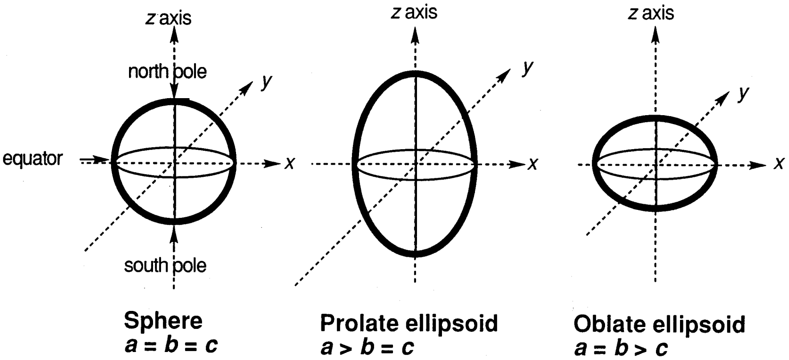


Fig. 5. A sphere, prolate ellipsoid, and oblate ellipsoid as examples of momental ellipsoids indicating the positions of the poles and the equator.

$$I=\sum_{i=1}^{n} m_i r_i^2 \tag{15}$$

in which m_i is the mass of particle i and r is the perpendicular distance of particle i from the axis in question. The locus of points at a distance $\sqrt{I}$ radially from the center of mass in the direction of the axis of rotation defines the surface of the momental ellipsoid, whose three mutually perpendicular axes coincide with the three principal axes of inertia of the molecule. In idealized coordination polyhedra with maximum possible symmetry and equal metal–ligand bond distances the principal axes of the momental ellipsoid correspond to the symmetry axes.

Let a, b, and c be the lengths of the three axes of this ellipsoid ordered so that $a \geq b \geq c$ and let the z axis be a rotation axis of the highest order present. If $a=b=c$ the momental ellipsoid is a sphere and the moment of inertia is the same about any axis through the center of mass (Fig. 5). The momental ellipsoids of the regular polyhedra, namely the tetrahedron, octahedron, cube, icosahedron, and I_h dodecahedron, are all spheres. Such regular polyhedra can therefore be called *spherical polyhedra*. If $a>b=c$ the momental ellipsoid is an elongated or prolate symmetric top with more density in the polar regions than the equatorial region and the corresponding polyhedra can be called *prolate polyhedra*. The atomic orbitals forming the hybrids for prolate polyhedra have relatively low $|m|$ values, i.e., are concentrated towards the z axis. Such atomic orbitals can be called *prolate orbitals*. On the other hand if $a=b>c$ the momental ellipsoid is a flattened or oblate symmetric top with more density in the equatorial region rather than the polar regions and the corresponding polyhedra can be called *oblate polyhedra*. The atomic orbitals forming the hybrids for oblate polyhedra have relatively high $|m|$ values, i.e., are concentrated in the equatorial plane. Such atomic orbitals can be called *oblate orbitals*. If all three axes of the momental ellipsoid are unequal ($a>b>c$), the momental ellipsoid is an asymmetric top. Coordination polyhedra containing at least one three-fold rotation axis, proper or improper, have momental ellipsoids which are symmetrical tops or spheres. However, a polyhedron of sufficiently low symmetry, even one with a C_3 axis such as the C_{3v} capped octahedron, can have sufficient degrees of freedom of vertex (ligand) movement without destroying its symmetry that it can be oblate, prolate, or even accidentally spherical.

3.3. Symmetry forbidden coordination polyhedra

Group-theoretical arguments can be used to exclude certain coordination polyhedra for a given manifold of valence atomic orbitals, at least if the presence of only two-electron two-center metal–ligand bonds is assumed [5]. The most conspicuous example is the exclusion of cubic coordination for the spherical sp^3d^5 manifold involved in most of transition metal coordination chemistry. Coordination polyhedra excluded by such symmetry considerations are conveniently called *symmetry forbidden coordination polyhedra*.

The group-theoretical demonstration that certain polyhedra are symmetry forbidden for a given manifold of valence atomic orbitals relates to the properties of these point groups of relatively high symmetry that can be considered as direct products of point groups of lower symmetry. This if the relevant groups of lower symmetry are designated as G with m operations E, $g_2,\ldots,g_m$ and H with n operations E, $h_2,\ldots h_n$ in which the operations of G and H are independent except for the identity, then the direct product $G \times H$ contains mn paired operations of the type EE, $g_2E,\ldots,g_mE$, Eh_2, $g_2h_2,\ldots g_mh_2$, $Eh_3,\ldots,g_{m-1}h_n$, g_mh_n where EE is the identity of $G \times H$ and where because of the independence of the operations of G and H, the order of the paired operations in $G \times H$ is immaterial [22]. The direct product $G \times H$ has the following properties:

1. If G has the r conjugacy classes $K_1 = E$, $K_2,\ldots,K_r$ and H has the s conjugacy classes $L_1 = E$, $L_2,\ldots,L_s$, then the direct product $G \times H$ has the rs conjugacy classes $K_1L_1 = E$, $K_2L_1,\ldots,K_rL_1$, K_1L_2, $K_2L_2,\ldots$, K_rL_2, $K_1L_3,\ldots,K_{r-1}L_s$, K_rL_s. The irreducible representations and their characters has a similar product structure.
2. The groups G and H are both normal subgroups of their direct product $G \times H$, where a normal subgroup is a subgroup consisting only of entire conjugacy classes.

Now consider the direct product structure of the symmetry point groups. In this connection a number of point groups can be expressed as direct products of the type $R \times C_s'$ where the factor group C_s' is either C_s $(E \oplus \sigma)$ or C_i $(E \oplus i)$ and R is a group consisting of only the identity and proper rotations, e.g., $C_{2v} = C_2 \times C_s$; $C_{2nh} = C_{2n} \times C_i = C_{2n} \times C_s$; $C_{(2n+1)h} = C_{2n+1} \times C_s$; $D_{2nh} = D_{2n} \times C_i = D_{2n} \times C_s$; $D_{(2n+1)h} = D_{2n+1} \times C_s$; $D_{(2n+1)d} = D_{2n+1} \times C_i$: $S_{4n+2} = C_{2n+1} \times C_i$; $T_h = T \times C_i$; $O_h = O \times C_i$; $I_h = I \times C_i$. Because of the direct product structure of these point groups, the non-identity element in the C_i or C_s factor group, conveniently called the *primary involution*, is in a class by itself. The character tables of these direct product point groups are $2r \times 2r$ matrices of the following type in which r is the number of classes in R and $\boldsymbol{X}$ is an $r \times r$ matrix corresponding to the character table of R:

$$\begin{pmatrix} X & X \\ X & -X \end{pmatrix} \tag{16}$$

In the character table (16) half of the characters for the primary involution are equal to the corresponding characters of the identity. The corresponding irreducible representations may be called the even or symmetrical irreducible representations since if the primary involution is an inversion, these irreducible representations are usually designated in character tables with a '*g*' for 'gerade'. The remaining half of the characters in (16) for the primary involution are the negative of the corresponding characters of the identity. The corresponding irreducible representations may be called the odd or antisymmetrical irreducible representations since if the primary involution is an inversion, these irreducible representations are normally designated in a character table with a '*u*' for 'ungerade.' A conclusion from these observations is that a reducible representation having a zero character for the primary involution must be the sum of an equal number of even and odd irreducible representations. More generally, let d^+ and d^- be the sums of the dimensions of the even and odd irreducible representations, respectively, forming the reducible representation having a character $\chi(S'')$ for the primary involution, S', so that

$$\chi(S') = d^+ - d^- \tag{17}$$

Let us apply these ideas to the spherical orbital manifolds of interest. For the nine-orbital sp^3d^5 manifold involved in most transition metal coordination chemistry, the s and d orbitals are even orbitals and the p orbitals are odd orbitals so that six of the nine orbitals are even and only the remaining three orbitals are odd. For an 8-vertex polyhedron whose symmetry point group is a direct product $R \times C_s'$, the character of the primary involution of the reducible representation corresponding to the vertex permutations under the symmetry point group is equal to the number of vertices which remain fixed when the primary involution is applied. If the primary involution is an inversion, as is the case for the full octahedral group O_h, its character is necessarily zero since no vertices of a polyhedron remain fixed when an inversion is applied since polyhedra do not have vertices at their inversion centers. Therefore, the reducible representation of an 8-vertex polyhedron with an inversion center contains equal numbers of even and odd irreducible representations. This corresponds to a hybridization using four symmetrical and four antisymmetrical atomic orbitals. Since only three orbitals of the sp^3d^5 manifold, namely the three p orbitals, are antisymmetrical, an 8-vertex polyhedron with an inversion center, such as the cube or hexagonal bipyramid, cannot be formed using only s, p, and d orbitals. Cubic and hexagonal bipyramidal coordination in discrete ML_8 complexes are thus only found in actinide coordination complexes using a valence orbital manifold containing f orbitals.

Related arguments can be applied to early transition metal hydrides and alkyls using the six-orbital sd^5 manifold where the s orbitals and all five d orbitals are gerade orbitals. Since the sd^5 manifold has no ungerade orbitals, *any* coordination polyhedra with an inversion center, including the regular octahedron, are symmetry-forbidden in this manifold. This argument can be used to rationalize the nonoctahedral geometries of d^0 early transition metal alkyls such as $W(CH_3)_6$ (Ref. [23]) and $Zr(CH_3)_6^{2-}$ (Ref. [24]).

4. Coordination polyhedra for the spherical sp^3d^5 nine-orbital manifold

4.1. The description of metal coordination by polyhedra

The choice of favored coordination polyhedra or even the assignment of a coordination polyhedron to a given chemical structure, would appear to be very complicated in view of the large number of topologically distinct polyhedra with even as few as seven vertices (Section 3.1). However, the properties of atomic orbitals coupled with an assumption of maximum symmetry for a given hybrid of atomic orbitals makes this problem both tractable and interesting. In my original work published in 1969, I selected coordination polyhedra with obviously high symmetry for various coordination numbers up to 9 and then used group theory methods to determine hybrids of atomic orbitals capable of forming the polyhedra in question [4]. In subsequent work, published 25 years later [7], I have studied the problem in the opposite manner, namely seeking the maximum symmetry polyhedron for a given hybrid of atomic orbitals. In the study of the spherical sp^3d^5 atomic orbital manifold important for transition metal coordination chemistry, this approach takes the following form:

1. Addition of one or two d orbitals to a four-orbital spherical sp^3 manifold to give five- and six-coordinate polyhedra, respectively;
2. Subtraction of one or two d orbitals from a nine-orbital spherical sp^3d^5 manifold to give eight- and seven-coordinate polyhedra, respectively.

The irreducible representations for the hybrid orbitals forming polyhedra of interest in transition metal coordination chemistry are listed in Table 4, where G refers to the symmetry point group; v, e, and f to the numbers of vertices, edges, and faces, respectively; and Γ_s to the irreducible representations and the corresponding atomic orbitals for the corresponding hybridization of the central metal atom.

4.2. Coordination number four

The only possible true polyhedron for coordination number four using all three p orbitals of the sp^3 manifold is the tetrahedron. Square planar four-coordination (e.g., in the xy plane) uses only two of the three p orbitals leading to $sp^2d(x^2-y^2)$ hybridization not involving the p_z orbital orthogonal to the xy plane. Square planar coordination is thus an extreme example of oblate coordination with all ligands in a single plane.

4.3. Coordination number five

The two possible polyhedra for coordination number five are the trigonal bipyramid for which the sp^3 manifold is supplemented by the prolate $d(z^2)$ orbital with two opposite major lobes and the square pyramid for which the sp^3 manifold is supplemented by the oblate $d(x^2-y^2)$ orbital with four coplanar major lobes. Both of these coordination polyhedra are found in five-coordinate ML_5 metal complexes [25]. The possibility of a continuous transformation of a trigonal bipyramid $sp^3d(z^2)$ hybrid to a square pyramid $sp^3d(x^2-y^2)$ hybrid through linear combinations of z^2 and x^2-y^2 orbitals can relate to the stereochemical non-rigidity of five-coordinate complexes by Berry pseudorotation processes [26–29]. In addition, the locations of the major lobes in a z^2 or an x^2-y^2 orbital is related to the geometry of the five-coordinate polyhedron arising when these d orbitals are added to the sp^3 hybrid of a tetrahedron. A tetrahedron has no more than three coplanar vertices and no pair of 'opposite' vertices, i.e., a pair of vertices connected by a straight line through the center so that the corresponding X–M–X angle is 180°. However, adding a z^2 orbital, which has two major lobes opposite each other, to an sp^3 hybrid generates the trigonal bipyramid in which there is a pair of opposite vertices, namely the two axial vertices. The trigonal bipyramid is a prolate polyhedron arising from the prolate z^2 orbital ($m=0$) added to the sp^3 manifold. Addition of an x^2-y^2 orbital with four coplanar major lobes to an sp^3 manifold generates the square pyramid, which has four coplanar vertices, namely the four basal vertices. The square pyramid is an oblate polyhedron arising from the oblate x^2-y^2 orbital added to the sp^3 manifold. Formation of a trigonal bipyramid or a square pyramid by addition of a z^2 or x^2-y^2 orbital, respectively, to an sp^3

Table 4
The irreducible representations for the hybrid orbitals corresponding to coordination polyhedra

Polyhedron	G	v	e	f	Γ_σ
Tetrahedron	T_d	4	6	4	$\mathrm{A_1(s)+T_2}(x,y,z)$
Square pyramid	C_{4v}	5	8	5	$\mathrm{2A_1}(\mathrm{s},z,z^2)+\mathrm{B_1}(x^2-y^2)+\mathrm{E}(x,y,xz,yz)$
Trigonal bipyramid	D_{3h}	5	9	6	$\mathrm{2A_1'}(\mathrm{s},z^2)+\mathrm{E'}(x,y,x^2-y^2,xy)+\mathrm{A_2''}(z)$
Trigonal prism	D_{3h}	6	9	5	$\mathrm{A_1'}(\mathrm{s},z^2)+\mathrm{E'}(x,y,x^2-y^2,xy)+\mathrm{A_2''}(z)+\mathrm{E''}(xz,yz)$
Pentagonal pyramid	C_{5v}	6	10	6	$\mathrm{2A_1}(\mathrm{s},z,z^2)+\mathrm{E_1}(x,y,xz,yz)+\mathrm{E_2}(x^2-y^2,xy)$
Octahedron	O_h	6	12	8	$\mathrm{A_{1g}(s)}+\mathrm{E_g}(z^2,x^2-y^2)+\mathrm{T_{1u}}(x,y,z)$
Capped octahedron	C_{3v}	7	15	10	$\mathrm{3A_1}(\mathrm{s},z,z^2)+\mathrm{2E}(x,y,x^2-y^2,xy,xz,yz)$
Pentagonal bipyramid	D_{5h}	7	15	10	$\mathrm{2A_1'}(\mathrm{s},z^2)+\mathrm{E_1'}(x,y)+\mathrm{E_2'}(x^2-y^2,xy)+\mathrm{A_2''}(z)$
4-Capped trigonal prism	C_{2v}	7	13	8	$\mathrm{3A_1}(\mathrm{s},z,z^2,x^2-y^2)+\mathrm{A_2}(xy)+\mathrm{2B_1}(x,xz)+\mathrm{B_2}(y,yz)$
Cube	O_h	8	12	6	$\mathrm{A_{1g}(s)}+\mathrm{T_{2g}}(xy,xz,yz)+\mathrm{A_{2u}}(\text{no s,p,d!})+\mathrm{T_{1u}}(x,y,z)$
3,3-Bicapped trigonal prism	D_{3h}	8	15	9	$\mathrm{2A_1'}(\mathrm{s},z^2)+\mathrm{E'}(x,y,x^2-y^2,xy)+\mathrm{2A_2''}(z)+\mathrm{E''}(xz,yz)$
Square antiprism	D_{4d}	8	16	10	$\mathrm{A_1}(\mathrm{s},z^2)+\mathrm{B_2}(z)+\mathrm{E_1}(x,y)+\mathrm{E_2}(x^2-y^2,xy)+\mathrm{E_3}(xz,yz)$
Bisdisphenoid 'D_{2d} dodecahedron')	D_{2d}	8	18	12	$\mathrm{2A_1}(\mathrm{s},z^2)+\mathrm{2B_2}(z,xy)+\mathrm{2E}(x,y,xz,yz)$
Tricapped trigonal prism	D_{3h}	9	21	14	$\mathrm{2A_1'}(\mathrm{s},z^2)+\mathrm{2E'}(x,y,x^2-y^2,xy)+\mathrm{A_2''}(z)+\mathrm{E''}(xz,yz)$
Capped square antiprism	C_{4v}	9	20	13	$\mathrm{3A_1}(\mathrm{s},z,z^2)+\mathrm{B_1}(x^2-y^2)+\mathrm{B_2}(xy)+\mathrm{2E}(x,y,xz,yz)$

manifold is a consequence of maximizing the overlap of the hybrid orbitals with the ligand orbitals at the vertices of these polyhedra.

Pentagonal planar coordination is a conceivable alternative to the trigonal bipyramid and square pyramid for coordination number five and is actually found, albeit with some distortion, in a few tellurium complexes of sulfur ligands such as the xanthato complex $[\mathrm{Te(S_2COEt)_3}]^-$ with one monodentate and two bidentate xanthato ligands [30]. Pentagonal planar coordination, like square planar coordination, can only use the two p orbitals that lie in the plane of the pentagon leading to $\mathrm{sp^2d^2}(x^2-y^2,xy)$ hybridization using the two d orbitals that have their major lobes in the plane of the pentagon. Pentagonal planar coordination is thus another extreme example of oblate coordination.

4.4. Coordination number six

There are four clearly distinguishable pairs of d orbitals that can be added to an $\mathrm{sp^3}$ hybrid to give a six-coordinate polyhedron, namely the pairs (x^2-y^2,z^2), (xz, z^2), (xy,x^2-y^2), and (xy,xz). Fig. 6 summarizes these pairs and the six-coordinate polyhedra that result from them.

The very symmetrical (O_h point group) regular octahedron is overwhelmingly favored for coordination number 6; it corresponds to the hybrid $\mathrm{sp^3d^2}(x^2-y^2,z^2)$ formed by adding the (x^2-y^2,z^2) pair of d orbitals to the $\mathrm{sp^3}$ hybrid. Note that the major lobes of the d orbitals involved in the octahedral hybrids are directed towards the vertices of the octahedron. Furthermore, the prolate z^2 orbital ($m=0$)

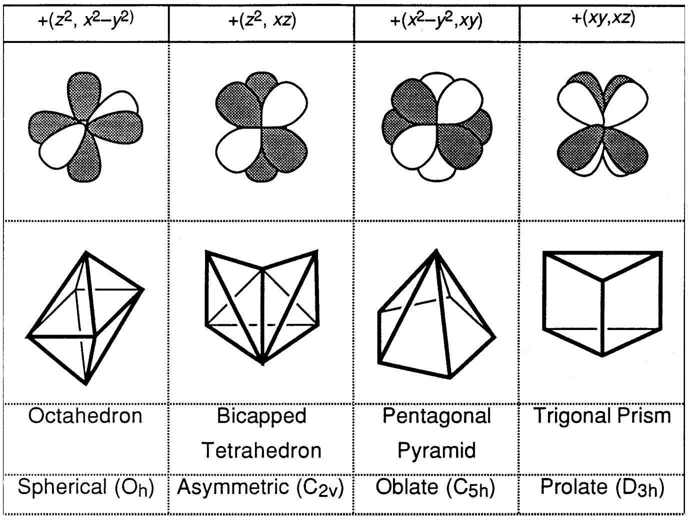


Fig. 6. The four distinguishable pairs of d orbitals that can be added to an $\mathrm{sp^3}$ manifold to give six-coordinate polyhedra.

exactly balances the oblate x^2-y^2 orbital ($m=2$) so that the octahedron is a spherical polyhedron consistent with its high symmetry with multiple C_3 and C_4 axes. The D_{3h} trigonal prism corresponding to $sp^3d^2(xz,yz)$ hybridization is found for tris(ethylenedithiolate) derivatives of early and middle transition metals [31]. The major lobes of the two d orbitals participating in trigonal prismatic hybridization are pointed towards the vertices although not as directly as in the case of the octahedron. A distorted pentagonal pyramid corresponding to $sp^3d^2(xy,x^2-y^2)$ hybridization is found for certain complexes of post-transition elements such as tellurium(IV) and antimony(III). The pentagonal pyramid is the only six-vertex polyhedron in which five of the vertices are coplanar; it is therefore not surprising that it is formed using the only pair of coplanar d orbitals which together have a total of eight coplanar major lobes. Since both the x^2-y^2 and xy orbitals are oblate ($m=2$ in both cases), the pentagonal pyramid is strongly oblate.

The final distinctive pair of d orbitals that can be added to an sp^3 manifold for a six-coordinate polyhedron is the (z^2,xz) pair corresponding to a bicapped tetrahedron similar to that found in the metal cluster $Os_6(CO)_{18}$ (Ref. [32]). This polyhedron as depicted is not favorable for a coordination polyhedron since the two capping vertices are further from the central metal atom than the remaining four vertices. However, the distortion of a regular $H_2M(CO)_2L_2$ octahedron towards an $M(CO)_2L_2$ tetrahedron in metal carbonyl dihydride derivatives of the type $H_2Fe(CO)_2L_2$ ($L=CO$ [33] and $PPh(OEt)_2$ [34]) is related to bicapped tetrahedral stereochemistry. The momental ellipsoid of the bicapped tetrahedron is asymmetric ($a \neq b \neq c$) in view of its relatively low symmetry (C_{2v}) and absence of a C_n or S_n axis of three or higher order.

4.5. Coordination number seven

The seven-coordinate polyhedron of maximum symmetry is the D_{5h} pentagonal bipyramid with $sp^3d^3(xy,x^2-y^2,z^2)$ hybridization. This polyhedron is commonly found in seven-coordinate complexes [35]. Other polyhedra found in seven-coordinate complexes include the capped octahedron with $sp^3d^3(z^2,xz,yz)$ or $sp^3d^3(z^2,xy,x^2-y^2)$ hybridization and the 4-capped trigonal prism with $sp^3d^3(z^2,xy,xz)$ or $sp^3d^3(x^2-y^2,xy,xz)$ hybridization. Note that the choice of d orbitals again affects the resulting coordination polyhedron (Fig. 7).

The orbital complement of the octahedron with $sp^3d^2(z^2,x^2-y^2)$ hybridization is a seven-vertex polyhedron with $sp^3d^3(xy,xz,yz)$ hybridization. However, there are no seven-vertex polyhedra with more than two symmetry elements which can be formed by $sp^3d^3(xy,xz,yz)$ hybrids. Nevertheless, the seven-orbital $sp^3d^3(xy,xz,yz)$ hybrid is of significance in being the unique sp^3d^3 manifold to which the $f(xyz)$ orbital (see Table 2) is added to form eight hybrid orbitals at the vertices of a cube (Fig. 8). In this sense, the octahedron is the orbital complement as well as the polyhedral dual of the cube. Note that the maximum electron density of an octahedron but the minimum electron density of the cube are located along the x, y, and z axes.

4.6. Coordination number eight

The common coordination polyhedra for coordination number eight [36–38] are the bisdisphenoid or 'D_{2d} dodecahedron' corresponding to sp^{3}d^4(z^2,xy,xz,yz) hybridization and the square antiprism corresponding to sp^{3}d^4(x^2-y^2,xy,xz,yz) hybridization (Fig. 8(a)). An oblate x^2-y^2 orbital with four major lobes is removed from the sp^{3}d^5 manifold to form the prolate bisdisphenoid. A prolate z^2 orbital with only two major lobes is removed from the sp^{3}d^5 manifold to form the oblate square antiprism. Removal of the prolate z^2 orbital from the sp^{3}d^5 manifold to form the oblate square antiprism sp^{3}d^4(x^2-y^2,xy,xz,yz) hybrid corresponds to removal of electron density from the midpoints of the square faces of the square antiprism through which the polar C_4/S_8 axis passes. Conversely removal of the oblate x^2-y^2 orbital from the sp^{3}d^5 manifold to form the prolate bisdisphenoid sp^{3}d^4(z^2,xy,xz,yz) hybrid corresponds to removal of electron density from the equatorial regions. Note that although the D_{2d} bisdisphenoid has no C_n axis where $n>2$, it has an S_4 axis leading to a symmetric rather than an asymmetric top for a momental ellipsoid. As in the case of five-coordinate complexes, the possibility of a continuous transformation of a bisdisphenoid sp^{3}d^4(z^2,xy,xz,yz) hybrid into a square antiprism sp^{3}d^4(x^2-y^2,xy,xz,yz) hybrid through linear combinations of 'missing' z^2 and x^2-y^2 orbitals can relate to the stereochemical non-rigidity of eight-coordinate complexes [39].

Similar ideas can be applied to the so-called 'forbidden' eight-coordinate polyhedra which cannot be formed by sp^{3}d^4 hybrids but which require sp^{3}d^{3}f hybrids, namely the cube, hexagonal bipyramid, and 3,3-bicapped trigonal prism (Fig. 9) [40]. The f orbitals required in the hybridization of these forbidden polyhedra relate to their shapes. For example, the f(xyz) orbital, with eight major lobes pointed

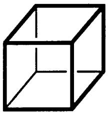
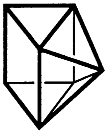
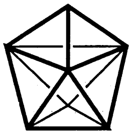
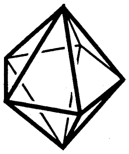
$-(z^2, x^2-y^2)$	$-(z^2, xz)$	$-(x^2-y^2, xy)$	$-(xy, xz)$
 Cube	 4-Capped Trigonal Prism	 Capped Octahedron	 Pentagonal Bipyramid
Addition of an $f(xyz)$ orbital is needed to give the 8 cubic hybrid orbitals		Also: 3-capped trigonal prism	Also: Capped octahedron; 4-capped trigonal prism; 3-capped trigonal prism

Fig. 7. The four distinguishable pairs of d orbitals that can be subtracted from an sp^{3}d^5 manifold to give seven-coordinate polyhedra.

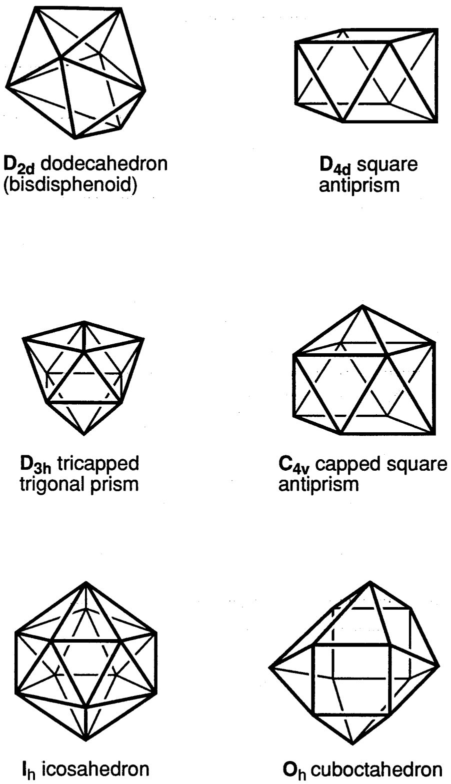


Fig. 8. (a) Eight-coordinate polyhedra which can be formed from sp^3d^4 hybrids; (b) nine-coordinate polyhedra that can be formed from sp^3d^5 hybrids; (c) Two highly symmetrical 12-coordinate polyhedra.

towards the vertices of a cube (Table 2), is used to form the sp^3d^3f hybrids of a cube, which is a spherical polyhedron in accord with its high symmetry and the exclusive use of d and f orbitals with $m = 1$ in its hybridization. An oblate $f(x(x^2 - 3y^2))$ orbital ($m = 3$) with six major lobes pointed towards the vertices of a regular hexagon is used for hexagonal bipyramidal hybridization, which is strongly oblate since six of its eight vertices are located in the equatorial plane. A prolate $f(z^3)$ orbital ($m = 0$) with its two major lobes along the z axis towards the two capping vertices (Table 2) is used to form the sp^3d^3f hybrids of a 3,3-bicapped trigonal prism, which is strongly prolate since two of its vertices are located at the poles and no vertices are located in the equatorial plane.

4.7. Coordination number nine

The deltahedron of maximum symmetry is the D_{3h} tricapped trigonal prism (Fig. 8(b)). Either this nine-vertex polyhedron or the nine-vertex capped square antiprism (Fig. 8(b)) can be formed using only a nine-orbital sp^3d^5 manifold and thus are feasible nine-vertex coordination polyhedra. The small number of nine-coordinate complexes including the hydrides [41,42] ReH_9^{2-} and TcH_9^{2-} generally use the tricapped trigonal prism.

5. Coordination polyhedra for other spherical manifolds of atomic orbitals

5.1. Coordination polyhedra for the four-orbital sp^3 manifold

The four-orbital sp^3 manifold (Table 3) is necessarily used by atoms below atomic number 10, since such atoms do not have energetically accessible d orbitals. In addition, the role of d orbitals in the chemical bonding of the heavier main group elements (post-transition elements) is questionable [43–45] since the nd orbitals are of significantly higher energy than the corresponding ns and np orbitals. For this reason the chemistry of post-transition elements may be rationalized using only a four-orbital sp^3 bonding manifold without d orbital participation. Coordination numbers 2, 3, and 4 for an sp^3 manifold necessarily exhibit linear, trigonal planar, and tetrahedral geometries, respectively, in the absence of stereochemically active lone pairs for coordination numbers 2 and 3. In the presence of stereochemically active lone pairs bent and pyramidal geometries are possible for coordination numbers 2 and 3, respectively. The only possible coordination geometry with an inversion center but without any multicenter bonding for an sp^3 manifold is linear two-coordination.

Coordination numbers five and six are possible for a four-orbital sp^3 manifold in so-called hypervalent compounds if three-center four-electron (3c–4e) bonds are used (Fig. 10, [43–45]). In such hypervalent compounds a single p orbital can form

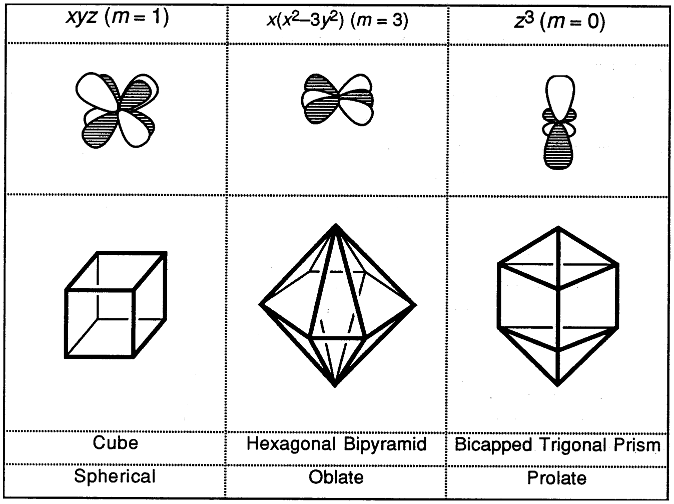


Fig. 9. Eight-coordinate polyhedra which cannot be formed from sp^3d^4 hybrids but which require sp^3d^4f hybridization indicating the shape of the required f orbital.

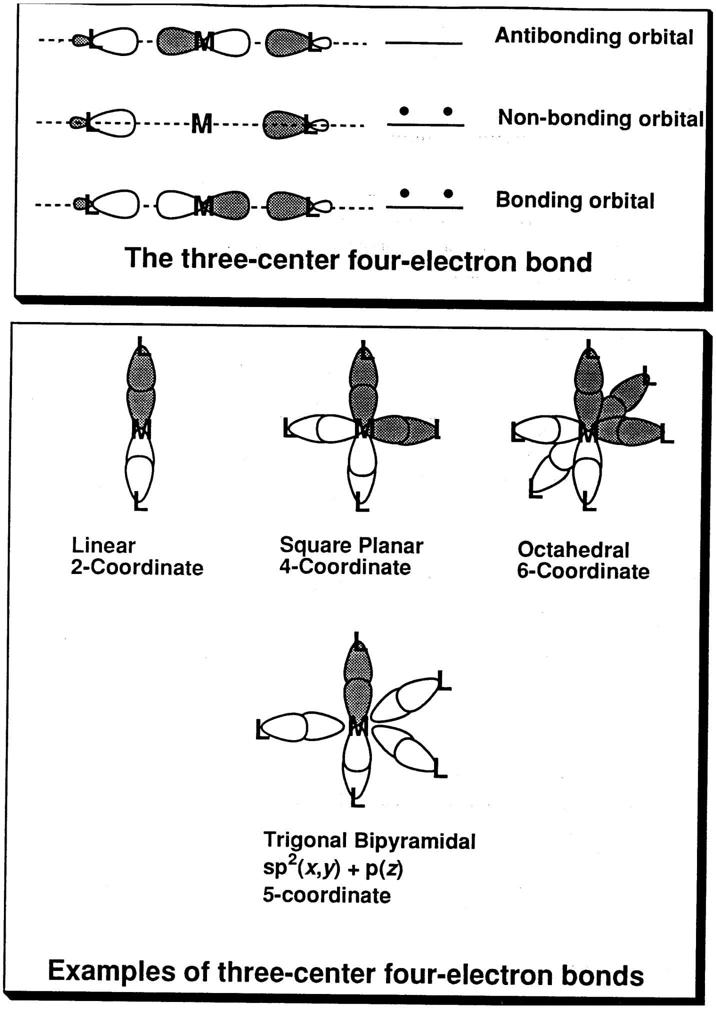


Fig. 10. The three-center four-electron bond.

a 3c–4e bond to two opposite ligands leading directly to two-coordinate linear complexes, four-coordinate square planar complexes, or six-coordinate octahedral complexes by involvement of one, two, or three p orbitals, respectively (Fig. 10). The involvement of d orbitals can be avoided in trigonal bipyramidal main group element compounds (e.g., PF_5) by forming the three equatorial bonds through $sp^2(x,y)$ hybrids and using the $p(z)$ orbital for a 3c–4e bond to the two axial ligands (Fig. 10). Coordination numbers higher than six are not feasible for a four-orbital sp^3 manifold even if 3c–4e bonds are used.

5.2. Coordination polyhedra for the six-orbital sd^5 manifold

The six-orbital sd^5 manifold (Table 3) may be found in simple homoleptic hydrides and alkyls of the early transition metals when the np orbitals are of significantly higher energy than the ns and $(n-1)$d orbitals [46]. The following bonding concepts have been proposed for such compounds:

1. Only s and d orbitals are used to form hybrid bond orbitals;
2. The hybrid orbitals have maximal s character (or sd^{n-1} hybridization when making n bonds);
3. Lone pairs are placed in pure d orbitals;
4. Three-center four-electron bonds similar to those in Fig. 10 are used when the central metal atom has more than 12 valence electrons.

Table 5 summarizes the possible shapes and corresponding hybridizations for the six-orbital sd^5 manifold up to the maximum coordination number of six. Some of the shapes of the resulting complexes are depicted in Fig. 11. Of particular interest is the fact that since the s orbital and all five d orbitals are gerade orbitals, an inversion center is not possible for coordination polyhedra using an sd^5 manifold with only two-electron two-center bonds. This has the following interesting consequences:

1. The octahedron and the trigonal prism both have inversion centers and are thus symmetry forbidden polyhedra for six-coordinate sd^5 metal complexes in the absence of multicenter bonding. This can rationalize the non-octahedral geometries of d^0 early transition metal alkyls such as $W(CH_3)_6$ (Ref. [23]) and $Zr(CH_3)_6^{2-}$ (Ref. [24]). The observed geometry for such structures as well as the

Table 5
The irreducible representations for the hybrid orbitals corresponding to configurations for coordination numbers three to six based on an sd^5 six-orbital manifold

Configuration	*G*	*v*	Γ_σ[a]
Trigonal Planar	D_{3h}	3	$A_1(s,z^2)+E'(x^2-y^2,xy)$
Trigonal Pyramidal	C_{3v}	3	$A_1(s,z^2)+E(x^2-y^2,xy;xz,yz)$
Tetrahedral	T_d	4	$A_1(s)+T_2(xy,xz,yz)$
Pyramidal	C_{3v}	4	$2A_1(s,z^2)+E(x^2-y^2,xy;xz,yz)$
Square Pyramid Base	C_{4v}	4	$A_1(s,z^2)+B_1(x^2-y^2)+E(xz,yz)$
Square Planar	$\mathbf{D_{4h}}$	**4**	$\mathbf{A_{1g}(s,z^2)+B_{1g}(x^2-y^2)+E_u(x,y)}$
Square Pyramid	C_{4v}	5	$2A_1(s,z^2)+B_1(x^2-y^2)+E(xz,yz)$
Pentagonal Pyramid Base	C_{5v}	5	$A_1(s,z^2)+E_1(xz,yz)+E_2(x^2-y^2,xy)$
Trigonal Bipyramid	$\mathbf{D_{3h}}$	**5**	$\mathbf{2A_1'(s,z^2)+E'(x^2-y^2,xy)+A_2''(z)}$
Pentagonal Pyramid	C_{5v}	6	$2A_1(s,z^2)+E_1(xz,yz)+E_2(x^2-y^2,xy)$
Distorted Trigonal Prism	C_{3v}	6	$2A_1(s,z^2)+2E(x^2-y^2,xy;xz,yz)$
Trigonal Prism	$\mathbf{D_{3h}}$	**6**	$\mathbf{A_1(s,z^2)+E'(x^2-y^2,xy)+A_2''(z)+E''(xz,yz)}$
Octahedron	$\mathbf{O_h}$	**6**	$\mathbf{A_1(s)+E_g(z^2,x^2-y^2)+T_{1u}(x,y,z)}$
Bicapped Tetrahedron	$\mathbf{C_{2v}}$	**6**	$\mathbf{3A_1(s,x^2-y^2,z^2)+B_1(xz)+2B_2(yz,y)}$

[a] Polyhedra listed in bold face require p orbitals in their hybridization. The required p orbitals are placed in boxes.

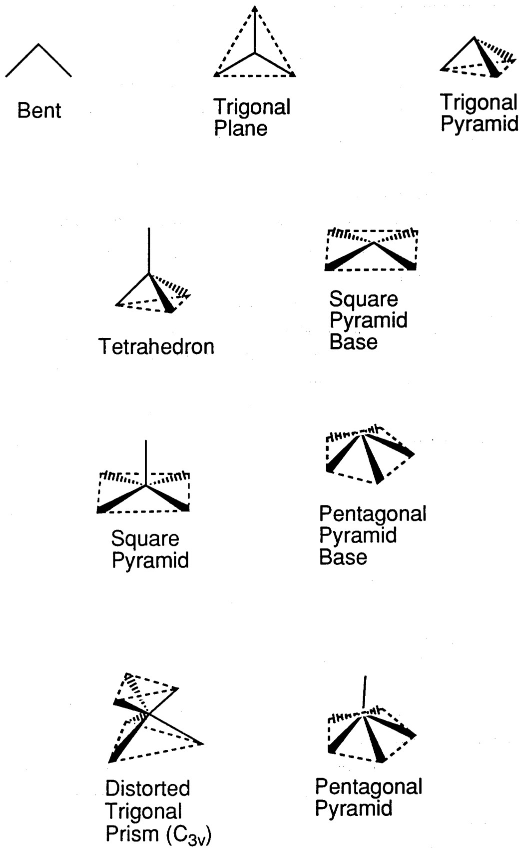


Fig. 11. Possible (i.e., symmetry allowed) shapes of early transition metal complexes using a six-orbital sd^5 manifold.

lowest energy calculated [47] structure for the hypothetical WH_6 appears to be a trigonal prism distorted from D_{3h} to C_{3v} symmetry in order to destroy its inversion center.

2. The trigonal bipyramid, although it does not have an rigorous inversion center, is symmetry forbidden for coordination number 5 using an sd^5 manifold. This may be a consequence of the fact that the two axial vertices of the trigonal bipyramid are related by an inversion center. The square pyramid is a feasible polyhedron for five-coordinate complexes using an sd^5 manifold and has been found experimentally [48,49] in $Ta(CH_3)_5$.
3. The planar square has an inversion center and thus is a forbidden geometry for four-coordinate complexes using an sd^5 manifold and only two-center bonding. A tetrahedron has no inversion center and thus is a favorable geometry for four-coordinate complexes using an sd^5 manifold.

5.3. Coordination polyhedra for the 13-orbital sd^5f^7 manifold

The 5f orbitals (Table 2) are not only energetically accessible valence orbitals for actinide chemistry [50,51] but are also of lower energy than the 7p orbitals so that the covalent bonding in most actinide derivatives [52] can be rationalized in terms of a thirteen-orbital sd^5f^7 manifold (Table 3). Table 6 summarizes possible hybridizations for selected polyhedra using a thirteen-orbital sd^5f^7 manifold with particular emphasis on polyhedra which cannot be formed using a nine-orbital sp^3d^5 manifold. The eight- and 12-vertex polyhedra listed in Table 6 are depicted in Figs. 8 and 9.

The following observations can be made concerning the information in Table 6:

1. Since the f orbitals are ungerade like the p orbitals all of the coordination polyhedra that are possible for a nine-orbital sp^3d^5 manifold (Table 4) are also possible for a thirteen-orbital sd^5f^7 manifold. In the hybridization schemes for such polyhedra the $\{x^3,y^3,z^3\}$ set of f orbitals (Table 2) plays a role analogous to the p orbitals. In addition, the cube and hexagonal pyramid (Fig. 9), which both have inversion centers, are forbidden for the sp^3d^5 manifold but are allowed for the sd^5f^7 manifold thereby rationalizing their occurrence in actinide chemistry.
2. For the sd^5f^7 manifold the largest polyhedra with inversion centers that can be formed have 12 vertices. These include the highly symmetrical icosahedron and cuboctahedron (Fig. 8(c)).

6. Summary

In this article, I have provide some examples, admittedly biased in favor of my own work, as to how some of the fundamental ideas on inorganic stereochemistry presented originally by Sidgwick and Powell in 1940 and developed subsequently by Gillespie and Nyholm in 1957 have evolved into a broad theoretical base for

Table 6
The irreducible representations for the hybrid orbitals corresponding to selected polyhedra for coordination numbers four to twelve based on an sd^5f^7 thirteen-orbital manifold

Polyhedron	G	v	e	f	Γ_σ
Tetrahedron	T_d	4	6	4	$A_1(s)+T_2(xy,xz,yz;x^3,y^3,z^3)$
Octahedron	O_h	6	12	8	$A_{1g}(s)+E_g(z^2,x-y^2)+T_{1u}(x^3,y^3,z^3)$
Cube	O_h	8	12	6	$A_{1g}(s)+T_{2g}(xy,xz,yz)+A_{2u}(xyz)+T_{1u}(x^3,y^3,z^3)$
Hexagonal Bipyramid	D_{6h}	8	18	12	$2A_g(s,z^2)+E_{2g}(xy,x^2-y^2)+A_{2u}(z^3)+B_{2u}[x(x^2-3y^2)]$ $+E_{1u}(xz^2,yz^2)$
Icosahedron	I_h	12	30	20	$A_g(s)+H_g(xy,xz,yz,x^2-y^2,z^2)+T_{1u}(x^3,y^3,z^3)$ $+T_{2u}[x(z^2-y^2),y(z^2-x^2),z(x^2-y^2)]$
Cuboctahedron	O_h	12	24	14	$A_{1g}(s)+E_g(z^2,x^2-y^2)+T_{2g}(xy,xz,yz)+T_{1u}(x^3,y^3,z^3)$ $+T_{2u}[x(z^2-y^2),y(z^2-x^2),z(x^2-y^2)]$

essentially all of coordination chemistry during the subsequent four decades. A variety of mathematical disciplines including group theory, graph theory, and topology have played a key role in this development. An essential aspect of this work has been a detailed understanding of the topology, shape, and symmetry of all of the actual and plausible polyhedra found in coordination chemistry and the relationship of such properties of the relevant polyhedra to those of the available atomic orbitals of the central metal atom. The improved understanding of the structure and bonding in coordination compounds arising from this theory is one of the more chemically significant results from the emerging discipline of mathematical inorganic chemistry [53–55].

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