Chemical Applications of Topology and Group Theory. 33. Symmetry-Forbidden Coordination Polyhedra for Spherical Atomic Orbital Manifolds[1]

R. B. King

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received February 12, 1997

The four chemically significant spherical manifolds of atomic orbitals are the sp^3, sd^5, sp^3d^5, and sd^5f^7 manifolds of 4, 6, 9, and 13 orbitals found in the chemistry of the main-group elements, the early transition metal homoleptic hydrides and alkyls, most other compounds of the d-block transition metals, and the actinides, respectively. Coordination geometries with an inversion center (e.g., the octahedron) or a unique reflection plane passing through no vertices (e.g., the trigonal prism) are symmetry forbidden for the sd^5 manifold thereby accounting for some unusual experimental and computed geometries for six-coordinate early transition metal hydrides and alkyls. The maximum coordination numbers for polyhedra with inversion centers for the nine-orbital sp^3d^5 and 13-orbital sd^5f^7 manifolds are 6 and 12 corresponding to the regular octahedron and regular icosahedron, respectively, for the most symmetrical manifestations of these coordination numbers.

1. Introduction

Spherical atomic orbital manifolds contain entire sets of atomic orbitals with a given value of the azimuthal quantum number, *l*, and are isotropic, i.e., they extend equally in all directions. The following spherical atomic orbital manifolds (Table 1) are of chemical interest: (a) the four-orbital sp^3 manifold ($l = 0$ and 1) involved in the chemistry of main-group elements including their hypervalent compounds; (b) the six-orbital sd^5 manifold ($l = 0$ and 2) involved in the chemistry of early transition metal hydrides and alkyls;[5] (c) the nine-orbital sp^3d^5 manifold ($l = 0$, 1, and 2) involved in the chemistry of the *d*-block transition metals; and (d) the 13-orbital sd^5f^7 manifold ($l = 0$, 2, and 3) involved in the chemistry of the actinides.

These manifolds are characterized by the following two numbers (Table 1): (a) 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; (b) 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. The group-theoretical basis for such symmetry-forbidden coordination polyhedra for the sp^3d^5 manifold was discussed in detail by the author in 1984.[6]

2. The Four-Orbital sp^3 Manifold

The four-orbital sp^3 manifold ($x = 4$, $y = 2$) 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[2−4] since the *n*d orbitals are of significantly higher energy than the corresponding *n*s and *n*p 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.

Table 1. Spherical Atomic Orbital Manifolds

manifold	elements involved	max. coordination no. (x)[a]	max. coordination no. with inversion center (y)[a]
sp^3	main group elements	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.

Coordination numbers 5 and 6are possible for a four-orbital sp^3 manifold in so-called hypervalent compounds if three-center four-electron bonds are used as suggested by Kutzelnigg,[2] Schleyer,[3] Buslaev,[4] and their co-workers. In such hypervalent compounds a single p orbital can 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. 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 three-center four-electron bond to the two axial ligands. Coordination numbers higher than 6

---

(1) Part 32: King, R. B. *Mol. Phys.* **1997**, *92*, 293.
(2) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.
(3) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.
(4) Buslaev, Ya. A.; Klyagina, A. P. *Coord. Chem. Rev.* **1993**, *126*, 149.
(5) Landis, C. R.; Cleveland, T.; Firman, T. K. *J. Am. Chem. Soc.* **1995**, *117*, 1859.
(6) King, R. B. *Theor. Chim. Acta* **1984**, *64*, 453.

S0020-1669(97)00156-0 CCC: $15.00

Table 2. The Irreducible Representations for the Hybrid Orbitals Corresponding to Configurations for Coordination Numbers 3−6 Based on an sd^5 Six-Orbital Manifold

configuration	group	v	$\Gamma_\sigma{}^a$
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**	$\mathbf{A_{1g}(s,z^2) + B_{1g}(x^2-y^2) + \underline{E_u(x,y)}}$
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**	$\mathbf{2A_1'(s,z^2) + E'(x^2-y^2,xy) + \underline{A_2''(z)}}$
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**	$\mathbf{A_1(s,z^2) + E'(x^2-y^2,xy) + \underline{A_2''(z)} + E''(xz,yz)}$
octahedron	$\mathbf{O_h}$	**6**	$\mathbf{A_1(s) + E_g(z^2,x^2-y^2) + \underline{T_{1u}(x,y,z)}}$
bicapped tetrahedron	$\mathbf{C_{2v}}$	**6**	$\mathbf{3A_1(s,x^2-y^2,z^2) + B_1(xz) + \underline{2B_2(yz,y)}}$

[a] Polyhedra listed in boldface require p orbitals in their hybridization. The required p orbitals are underlined.

are not feasible for a four-orbital sp^3 manifold even if three-center four-electron bonds are used.

3. The Six-Orbital sd^5 Manifold

The six-orbital sd^5 manifold ($x = 6$, $y = 0$) may be found in simple homoleptic hydrides and alkyls of the early transition metals when the *n*p orbitals are of significantly higher energy than the *n*s and ($n - 1$)d orbitals. The following bonding concepts have been proposed by Landis and co-workers[5] for such compounds: (a) only s and d orbitals are used to form hybrid bond orbitals; (b) the hybrid orbitals have maximal s character (or sd^{v-1} hybridization when making v bonds). (c) lone pairs are placed in pure d orbitals. (d) Three-center four-electron bonds are used when the central metal atom has more than 12 valence electrons.

Table 2 summarizes the possible shapes and corresponding hybridizations for the six-orbital sd^5 manifold up to the maximum coordination number of 6. Some of the shapes of the resulting complexes are depicted in Figure 1. Of particular interest is the fact that since the s orbital and all five d orbitals are gerade orbitals (i.e., $y = 0$), 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:

(a) The octahedron has an inversion center. The trigonal prism does not have an inversion center but has a unique reflection plane passing through no vertices (i.e., σ_h, which is a primary plane[6] fixing zero vertices). The octahedron and the trigonal prism are thus both symmetry forbidden[6] for six-coordinate sd^5 metal complexes in the absence of multicenter bonding. This can rationalize the nonoctahedral geometries of d^0 early transition metal alkyls such as $W(CH_3)_6$ (ref 7) and $Zr(CH_3)_6{}^{2-}$ (ref 8). The observed geometry for such structures as well as the lowest energy calculated[9] 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.

(b) The trigonal bipyramid, although it does not have an 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[10,11] in $Ta(CH_3)_5$.

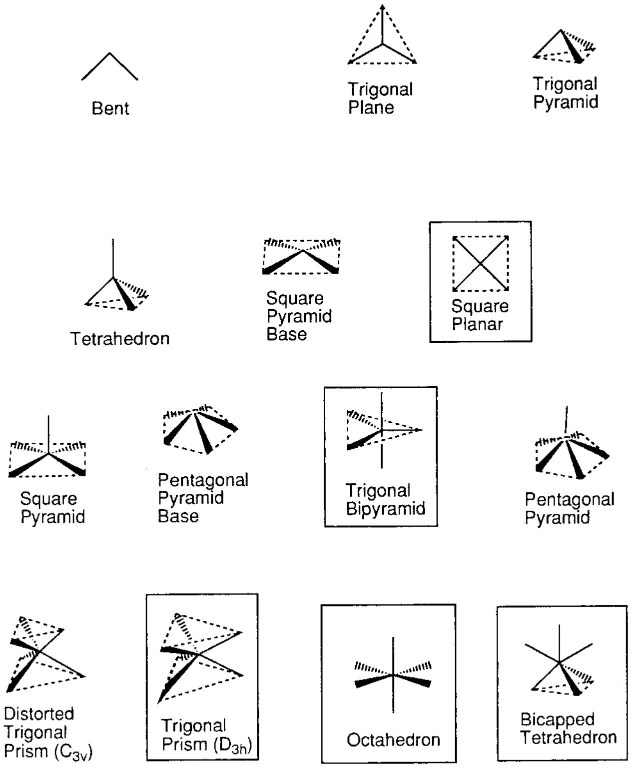

Figure 1. Configurations listed in Table 2 for a six-orbital sd^5 manifold. Configurations enclosed in boxes (e.g., square planar, trigonal bipyramid, trigonal prism, octahedron, and bicapped tetrahedron) are not possible using only s and d orbitals without the involvement of p orbitals or multicenter bonding.

(c) 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.

Known homoleptic transition metal hydrides[12] with more than 12 metal valence electrons (including lone pairs) like the square

---

(7) Haaland, A.; Hammel, A.; Rypdal, K.; Volden, H. V. *J. Am. Chem. Soc.* **1989**, *112*, 4547.

(8) Morse, P. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 4114.

(9) Shen, M.; Schaefer, H. F., III; Partridge, H. *J. Chem. Phys.* **1993**, *98*, 508.

(10) Albright, T. A.; Tang, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1462.

(11) Pulham, C.; Haaland, A.; Hammel, A.; Rypdal, K.; Verne, H. P.; Volden, H. V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1464.

(12) Bronger, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 759.

Table 3. The Irreducible Representations for the Hybrid Orbitals Corresponding to Selected Polyhedra for Coordination Numbers 4−12 Based on an sd^5f^7 13-Orbital Manifold

polyhedron	group	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	$A_{1g}(s) + E_g(z^2,x^2-y^2) + T_{1u}(x^3,y^3,z^3)$
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	$A_g(s) + Hg(xy,xz,yz,x^2-y^2,z^2) + T_{1u}(x^3,y^3,z^3) + T_{2u}[x(z^2-y^2),y(z^2-x^2),z(x^2-y^2)]$
cuboctahedron	O_h	12	24	14	$A_{1g}(s) + E_g(z^2,x^2-y^2) + T_{2g}(xy,xz,yz) + T_{1u}(x^3,y^3,z^3) + T_{2u}[x(z^2-y^2),y(z^2-x^2),z(x^2-y^2)]$

planar MH_4^{2-} ($M = Pd$,[13] Pt[14,15]) and the octahedral FeH_6^{4-} have the same geometries as other PtX_4^{2-} and FeX_6^{4-} complexes (e.g., X = CN) and thus are normally formulated as 16- and 18-electron complexes, respectively, with p orbital participation in the sp^3d^5 valence orbital manifold discussed below. However, alternative interpretations of these complexes without p orbital participation but with four-electron three-center bonds can be considered analogous to the four-electron three-center bonding in the hypervalent main group element complexes.[2−4] The number of four-electron three-center bonds (4C3EB) in these complexes using six-orbital sd^5 manifolds can be related to the number of metal valence electrons (VE) by the following equation:

$$4C3EB = {}^1\!/_2(VE - 12)$$

Possible structures of this type include the 14-electron $D_{\infty h}$ linear complexes PdH_2^{2-},[16,17] hypothetical C_{2v} T-shape PdH_3^-, and hypothetical C_{2v} sawhorse RhH_4^- with a single four-electron three-center bond, the 16-electron D_{4h} square planar complexes RhH_4^{3-} (ref 18) and MH_4^{2-} ($M = Pd$,[13] Pt,[14,15]) and hypothetical C_{4v} square pyramidal complex RhH_5^{2-} with two orthogonal four-electron three-center bonds, and the 18-electron O_h octahedral complexes ReH_6^{5-} (ref 19), MH_6^{4-} ($M = Fe$,[20] Ru,[21] Os[22]), $M'H_6^{3-}$ (M′ = Rh, Ir),[23] and PtH_6^{2-} (refs 24 and 25) with three orthogonal four-electron three-center bonds. Homoleptic late transition metal hydride anion structures with metal coordination numbers below 6 and an 18-electron configuration such as C_{4v} square pyramidal CoH_5^{4-} (ref 26) as well as tetrahedral CoH_4^{5-} (ref 27) and NiH_4^{4-} (refs 28−30) cannot be formed using a six-orbital sd^5 manifold and three-center four-electron bonds and thus necessarily must use p orbitals of the late transition metal in the nine-orbital sp^3d^5 manifold discussed below.

4. The Nine-Orbital sp^3d^5 Manifold

This nine-orbital sp^3d^5 manifold ($x = 9$, $y = 6$) has been discussed in detail by the author,[31−33] and by Mingos and Lin Zhenyang[34] since it is the usual valence-orbital manifold for the extensive chemistry of the d-block transition metals except for some of the early transition metals as noted above. In this manifold several rather symmetrical eight-vertex coordination polyhedra (e.g., the cube and hexagonal bipyramid) are symmetry forbidden because they have inversion centers.[6]

5. The 13-Orbital sd^5f^7 Manifold

The 5f orbitals[35,36] not only are energetically accessible valence orbitals for actinide chemistry[37,38] but also are of lower energy than the 7p orbitals so that the covalent bonding in most actinide derivatives[39] can be rationalized in terms of a 13-orbital sd^5f^7 manifold ($x = 13$, $y = 12$). Table 3 summarizes possible hybridizations for selected polyhedra using a 13-orbital sd^5f^7 manifold with particular emphasis on polyhedra which cannot be formed using a nine-orbital sp^3d^5 manifold.

The following observations can be made concerning the sd^5f^7 manifold:

(a) 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 are also possible for a 13-orbital sd^5f^7 manifold. In the hybridization schemes for such polyhedra, the $\{x^3,y^3,z^3\}$ set of f orbitals[35,36] plays a role analogous to that of the p orbitals. In addition, the cube and hexagonal pyramid, which of 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.

(b) 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.

IC9701569

---

(13) Bronger, W.; Auffermann, G. *J. Alloys Compd.* **1992**, *187*, 87.
(14) Bronger, W.; Müller, P.; Schmitz, D.; Spittank, H. *Z. Anorg. Allg. Chem.* **1984**, *516*, 35.
(15) Bronger, W.; Auffermann, G.; Müller, P. *J. Less-Common Met.* **1988**, *142*, 243.
(16) Bronger, W.; Auffermann, G. *J. Less-Common Met.* **1990**, *158*, 163.
(17) Bronger, W.; Jansen, K.; Müller, P. *J. Less-Common Met.* **1990**, *161*, 299.
(18) Bronger, W.; Müller, P.; Kowalczyk, J.; Auffermann, G. *J. Alloys Compd.* **1991**, *176*, 263.
(19) Huang, B.; Yvon, K.; Fischer, P. *J. Alloys Compd.* **1993**, *197*, 97.
(20) Didisheim, J.-J.; Zolliker, P.; Yvon, K.; Fischer, P.; Schefer, J.; Gubelmann, M.; Williams, A. F. *Inorg. Chem.* **1984**, *23*, 1953.
(21) Huang, B.; Yvon, K.; Fischer, P. *J. Alloys Compd.* **1994**, *210*, 243.
(22) Huang, B.; Bonhomme, F.; Selvam, P.; Yvon, K.; Fischer, P. *J. Less-Common* **1991**, *171*, 301.
(23) Bronger, W.; Gehlen, M.; Auffermann, G. *J. Alloys Compd.* **1991**, *176*, 255.
(24) Bronger, W.; Auffermann, G. *Angew. Chem., Int. Ed.* **1994**, *33*, 1112.
(25) Bronger, W. *J. Alloys Compd.* **1995**, *219*, 45.
(26) Zolliker, P.; Yvon, K.; Fischer, P.; Schefer, J. *Inorg. Chem.* **1985**, *24*, 4177.
(27) Černý, R.; Bonhomme, F.; Yvon, K.; Fischer, P.; Zolliker, P.; Cox, D. E.; Hewat, A. *J. Alloys Compd.* **1992**, *187I, 233.*
(28) Zolliker, P.; Yvon, K.; Jorgensen, J. D.; Rotella, F. J. *Inorg. Chem.* **1986**, *25*, 3590.
(29) Huang, B.; Yvon, K.; Fischer, P. *J. Alloys Compd.* **1992**, *178*, 173.
(30) Huang, B.; Yvon, K.; Fischer, P. *J. Alloys Compd.* **1994**, *204*, L5.
(31) King, R. B. *Applications of Graph Theory and Topology in Inorganic Cluster and Coordination Chemistry*; CRC Press: Boca Raton, FL, 1993; Chapter 3.
(32) King, R. B. *Polyhedron* **1994**, *13*, 2005.
(33) King, R. B. *J. Chem. Educ*. **1996**, *73*, 993.
(34) Mingos, D. M. P.; Lin Zhenyang. *Struct. Bonding* **1990**, *72*, 73.
(35) Freedman, H. G., Jr.; Choppin, G. R.; Feuerbacher, D. G. *J. Chem. Educ.* **1964**, *41*, 354.
(36) Becker, C. *J. Chem. Educ.* **1964**, *41*, 358.
(37) Walch, P. F.; Ellis, D. E. *J. Chem. Phys.* **1976**, *65*, 2387.
(38) Boring, M.; Wood, J. H. *J. Chem. Phys.* **1979**, *17*, 392.
(39) King, R. B. *Inorg. Chem.* **1992**, *31*, 1978.