netium signal. This follows from the relationship of line width to the radius of the molecule; the bulkier the molecule, the greater the line width.[12]

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Chemical Applications of Topology and Group Theory. 27. Covalent Bonding in Actinide Derivatives[1a]

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The d-block transition metals are characterized by forming strong covalent bonds involving the d orbitals in a nine-orbital spherical sp^3d^5 manifold thereby leading to the familiar "18-electron rule" for the stable electronic configurations of transition metal coordination and organometallic complexes.[2] On the other hand the 4f orbitals in the lanthanides appear to participate very little in covalent bond formation so that the chemistry of the lanthanides is governed largely by electrostatic considerations similar to the chemistry of the alkali and alkaline earth metals but with a predominant +3 oxidation state. The chemistry of the actinides from at least uranium through americium exhibits some features of both the predominantly covalent bonding of the d-block transition metals and the predominantly electrostatic bonding of the lanthanides since both the 5f and 6d orbitals of the actinides can function as valence orbitals leading to an unusual 12-orbital spherical d^5f^7 manifold.[3,4] This paper uses elementary group theory to explore how such a d^5f^7 manifold can participate in the types of covalent bonding prevalent in actinide chemistry. The d^5f^7 valence orbital manifold is also of interest in violating the frequent assumption of "minimum valence orbital nodality" by using binodal d orbitals and trinodal f orbitals in preference to uninodal p orbitals; this assumption, for example, was implicit in a survey of coordination polyhedra by the author[5] about 20 years ago in the first paper of this series. This work also represents an extension of some ideas first outlined by Eisenstein[6] in 1956.

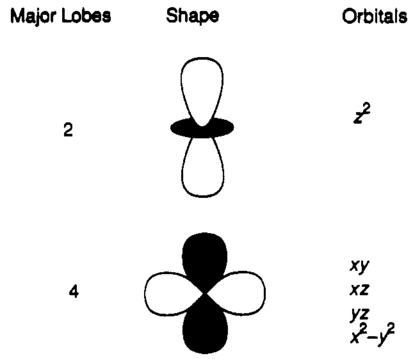

Figure 1. Shapes of the d orbitals showing the number of major lobes. The total number of major lobes in the standard set of five d orbitals is (1)(2) + (4)(4) = 18.

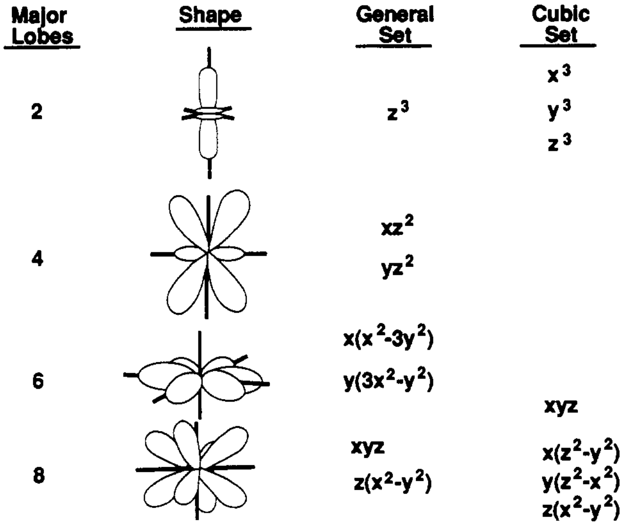

Figure 2. General shapes of both the general and cubic sets of f orbitals showing the numbers of major lobes. The total number of major lobes in either set of seven f orbitals is (1)(2) + (2)(4) + (2)(6) + (2)(8) = (3)(2) + (4)(8) = 38.

Covalently bonded actinide derivatives have been subjects of a number of computational studies.[7] The actinyl ions, particularly UO_2^{2+}, have been treated by a number of diverse methods including ligand field theory,[8] relativistic extended Hückel methods,[9–12] relativistic Xα methods,[13–15] and ab initio Hartree–Fock methods using Slater[16] or Gaussian[17,18] orbitals including relativistic effects in the latter, much more modern, computations. In addition, cyclopentadienylactinide compounds have been studied by Tatsumi and collaborators[19–23] using the extended Hückel method and by Bursten and co-workers[24–27] using Xα–SW molecular orbital calculations with quasirelativistic corrections. The uranium–uranium bonding in the dimer U_2 has been studied by both relativistic Xα–SW molecular orbital calculations[28] and relativistic Gaussian ab initio methods.[29] Quasirelativistic Xα–SW

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Table I. Axial Symmetry of Orbitals in the d^5f^7 Manifold for Actinide Covalent Bonding

σ-bonding (zero axial nodes)	dσ: z^2	fσ: z^3
π-bonding (one axial node)	dπ: xz, yz	fπ: xz^2, yz^2
δ-bonding (two axial nodes)	dδ: xy, $x^2 - y^2$	fδ: $z(x^2 - y^2)$, xyz
φ-bonding (three axial nodes)	none	fφ: $x(x^2 - 3y^2)$, $y(3x^2 - y^2)$

molecular calculations have also been used[30] to study the uranium–uranium interactions in the uranium(V) alkoxides $U_2(OR)_{10}$. This paper explores what can be learned about covalent bonding in actinide chemistry by using simple group theory without undertaking such complicated computations which at times have given confusing and even conflicting results.[31,32]

Figure 1 depicts the familiar five d orbitals in a manner which is used in Figure 2 to depict both the cubic and general sets of seven f orbitals.[33-36] Note that the set of five d orbitals (Figure 1) has a total of 18 major lobes, namely two from the z^2 orbital and four from each of the $x^2 - y^2$, xy, xz, and yz orbitals. In an analogous manner either set of f orbitals (cubic or general) has a total of 38 major lobes, partitioned as indicated in Figure 2.

Many of the configurations of interest in actinide chemistry, including $AnO_2^{+/2+}$ and $(C_8H_8)_2An$ as well as cubic and hexagonal bipyramidal coordination, are centrosymmetric; i.e., they have centers of inversion in their symmetry point groups. The valence orbitals forming such centrosymmetric configurations must consist of equal numbers of gerade and ungerade orbitals. In the case of a d^5f^7 manifold in which the d orbitals are the gerade orbitals and the f orbitals are the ungerade orbitals, only 10 of the 12 orbitals of the manifold, namely the five d orbitals and only five of the seven f orbitals, can be involved in the chemical bonding of a centrosymmetric structure, thereby making two of the seven f orbitals inaccessible for covalent bonding but available for extra metal electrons. This is exactly what occurs in the bonding in the actinocenes $(C_8H_8)_2An$, as will be seen below. An exactly analogous situation prevents centrosymmetric eight-vertex polyhedra, such as the cube and hexagonal bipyramid, from being formed by a nine-orbital sp^3d^5 manifold, which contains only three ungerade orbitals, namely the three p orbitals.[37]

Many actinide derivatives are characterized by strong covalent bonding in a single axial direction and only weak electrostatic bonding (if any) in the other two directions. Important examples include actinyl derivatives $AnO_2^{+/2+}$ having strong axial bonds to oxygen[38] and the actinocenes, $(C_8H_8)_2An$, having strong axial bonds to planar C_8H_8 rings.[39] In order to understand the actinide covalent bonding in such derivatives, it is necessary to understand the symmetries of the 12 orbitals of the actinide d^5f^7 manifold from the point of view of the axially bonded atom or ring. These are depicted in Table I in which the axis of the strong covalent bonds is taken to be the z axis. Note that factoring $z^{(n-n_{ax})}$ where n is the total orbital nodality (i.e., $n = 2$ and 3 for d and f orbitals, respectively) and n_{ax} is the axial nodality (i.e., $n_{ax} = 0$, 1, 2, and 3 for σ, π, δ, and φ bonding, respectively) out of the designations of the d and f orbitals leads to designations of atomic orbitals of lower nodalities exhibiting the same symmetry towards the axial atom. Table I also uses the shortened notations dσ, dπ, dδ, fσ, fπ, fδ, and fφ to represent d and f orbitals of the indicated symmetries relative to the axially bonded atom or ring.

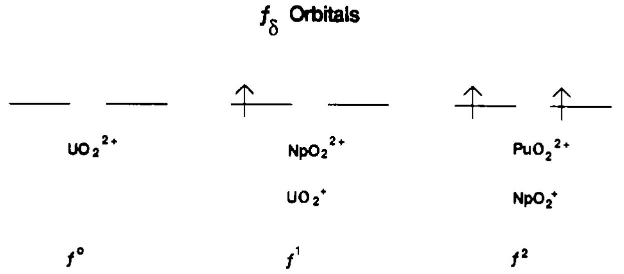

Figure 3. Electron occupancy of the fδ orbitals in the f^0 actinyl ion UO_2^{2+}, the f^1 actinyl ions NpO_2^{2+} and UO_2^+, and the f^2 actinyl ions PuO_2^{2+} and NpO_2^+.

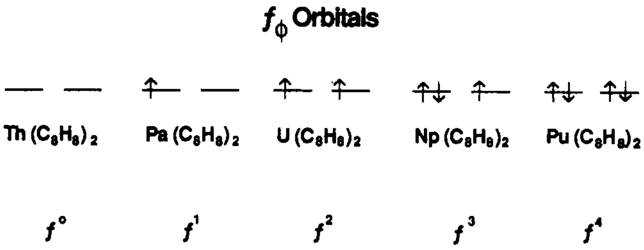

Figure 4. Electron occupancy of the fφ orbitals in the actinocenes $An(C_8H_8)_2$ (An = Th, Pa, U, Np, Pu).

The actinyl ions AnO_2^{2+} (An = U, Np, Pu, Am) are characterized by very short (~1.7–1.8 Å for UO_2^{2+}) axial actinide–oxygen bonds; these ions readily form complexes containing four to six weakly bonded ligands in equatorial positions.[40] Table I shows how the strong axial metal–oxygen bonds in the actinyl ions can be formulated as triple bonds with one σ component and two orthogonal π components using orbitals in the d^5f^7 manifold according to the following scheme: σ–bonding, linear actinide $d(z^2)f(z^3)$ hybrids overlapping with linear oxygen sp(z) hybrids; π-bonding, two orthogonal π-bonds using actinide $d^2(xy,yz)$-$f^2(xy^2,yz^2)$ hybrids overlapping with oxygen p orbitals. The oxygen lone pair in the sp hybrid directed away from the actinide can serve as a ligand to another metal atom in polynuclear complexes or in solid-state structures of uranates.[41]

This bonding model for the actinyl ions AnO_2^{2+} uses a six-orbital d^3f^3 subset of the d^5f^7 manifold for two triple bonds to the axial oxygens. Among the remaining orbitals of the d^5f^7 manifold, the two dδ and two fφ orbitals have appreciable electron density in the equatorial plane, and thus like the less energetically accessible 7p(x) and 7p(y) orbitals can interact strongly with the equatorial ligands, thereby being pushed to antibonding energy levels in a standard ligand field approach.[42] This leaves the two degenerate fδ orbitals, which have the xy plane as a nodal plane, as nonbonding orbitals which can receive actinide electrons. The fδ orbitals are thus empty in f^0 UO_2^{2+}, contain one unpaired electron in the f^1 ions UO_2^+ and NpO_2^{2+}, and are half-filled with two unpaired electrons in the f^2 ions NpO_2^+ and PuO_2^{2+} (Figure 3). Special stability of the half-filled fδ orbitals in the f^2 ions can rationalize certain observations in actinide aqueous solution chemistry such as the greater aqueous stability of the f^2 NpO_2^+ relative to f^1 UO_2^+ or f^3 PuO_2^+ and the lower oxidizing power of f^2 PuO_2^{2+} relative to f^1 NpO_2^{2+}.[43]

The actinocenes, $(C_8H_8)_2An$ (An = Th, Pa, U, Np, Pu) are very thermally stable organometallic derivatives which in some cases (e.g., An = U, Np, Pu) are unreactive toward water in the absence of oxygen.[39,44] The coaxial actinide–ring bonds may be regarded as strong covalent bonds and involve donation of 10

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Table II. Use of the Actinide d^5f^7 Valence Orbital Manifold for δ-Bonding and π-Bonding in T_d $(C_5H_5)_4An$ Derivatives

	d orbitals	cubic f orbitals
σ-bonds (4)		
A		fβ: xyz
T_2	dγ: xy, xz, yz	fδ: x^3, y^3, z^3
π-bonds (8)		
E	dε: $x^2 - y^2, z^2$	
T_1		fε: $x(y^2 - z^2), y(z^2 - x^2), z(x^2 - y^2)$
T_2	dγ: xy, xz, yz	fδ: x^3, y^3, z^3

electrons from each planar $C_8H_8^{2-}$ *dianion* to the actinide to have one σ component, two orthogonal π components, and two δ components displaced by 45° using the following scheme: σ-bonding, electron donation from filled anodal ring a_1 orbitals to empty linear actinide $d(z^2)f(z^3)$ hybrid orbitals; π-bonding, two orthogonal π bonds involving electron donation from filled uninodal ring e_{1u} orbitals to empty actinide $d^2(xz,yz)f^2(xz^2,yz^2)$ hybrid orbitals; δ-bonding, two δ-bonds at 45° angles to each other involving electron donation from filled binodal ring e_2 orbitals to empty actinide $d^2(xy,x^2 - y^2)f^2(z(x^2 - y^2)xyz)$ hybrid orbitals. The remaining two f orbitals, namely the two degenerate fϕ orbitals (Table I), when occupied by actinide f electrons, can stabilize further the already quintuple metal–ring bond by back-donation into the empty antibonding trinodal ring e_3 orbitals using a trinodal ϕ bond. This ϕ back-bonding, although relatively weak, may contribute to the aqueous stability of f^2 $(C_8H_8)_2U$, f^3 $(C_8H_8)_2Np$, and f^4 $(C_8H_8)_2Pu$ relative to f^0 $(C_8H_8)_2Th$. Such ϕ back-bonding can stabilize the f orbitals, which are occupied by 0, 1, 2, 3, and 4 electrons in the Th, Pa, U, Np, and Pu, derivatives, respectively, as depicted in Figure 4 leading to the observed 0, 1, 2, 1, and 0 unpaired electrons, respectively, in accord with the observed magnetic properties.[39,44,45] Note also that $(C_8H_8)_2Pu$ has a filled d^5f^7 manifold analogous to the filled sp^3d^5 manifold of $(C_5H_5)_2Fe$. This suggests a special stability of $(C_8H_8)_2Pu$ relative to the other actinocenes, which may be reflected in more extensive ring chemistry of $(C_8H_8)_2Pu$ without decomposition relative to the other $(C_8H_8)_2An$ derivatives. This possibility remains to be tested experimentally.

The tetracyclopentadienylactinides, $(C_5H_5)_4An$ (An = Th, Pa, U, Np), are very stable derivatives[46,47] in which each actinide–ring bond may be regarded as a triple bond having one σ component and two orthogonal π components similar to the iron–ring bonds in ferrocene.[48] The central actinide in the tetracyclopentadienylactinides, $(C_5H_5)_4An$, forms a total of four σ-bonds and eight π-bonds to the four C_5H_5 rings leading to a total of (4)(3) = 12 bonds. Table II shows how the twelve orbitals from the d^5f^7 manifold of the central actinide have exactly the correct symmetries for these 12 bonds in $(C_5H_5)_4An$ derivatives. Because of the 3-fold degeneracies of some of the irreducible representations in the T_d point group, the cubic set of f orbitals[33,34] rather than the general set of f orbitals is used so that the significance of the fδ designation in Table II is totally different from that in Table I. Note also that a tetrahedron is not centrosymmetric so that seven ungerade f orbitals can be used in conjunction with only five gerade d orbitals for the four metal–ring triple bonds in the $(C_5H_5)_4An$ derivatives. The central actinide atoms in other cyclopentadienylactinide derivatives of the general formula Cp_3AnX (Cp = cyclopentadienyl or substituted cyclopentadienyl; An = Th, U, Np; X = halide, alkyl, etc.)[44] can use subsets of the d^5f^7 actinide valence orbital manifold omitting appropriate orbitals when cyclopentadienyl groups are replaced by groups not forming both orthogonal π-bonds in addition to a σ-bond.

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