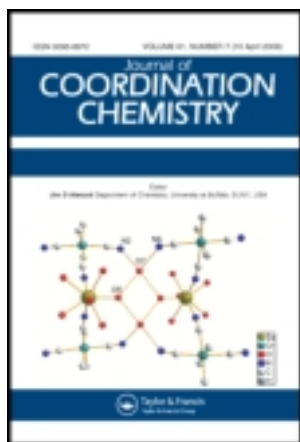


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Coordination chemistry in two dimensions: the angular overlap model for actinyl complexes

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Coordination chemistry in two dimensions: the angular overlap model for actinyl complexes†

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The angular overlap model has been applied to the study of actinyl coordination complexes AnO_2L_n ($\text{An} = \text{U}, \text{Np}, \text{Pu}, \text{Am}; n = 4, 5, 6$) using a 13-orbital sd^5f^7 manifold. After allowing for a triply bonded ($\sigma + 2 \perp \pi$) linear $\text{O} \equiv \text{An} \equiv \text{O}$ substructure, a seven-orbital submanifold $\text{d}^3\{\text{d}\sigma, \text{d}\delta\}\text{f}^4\{\text{f}\delta, \text{f}\phi\}$ remains for σ and π bonding to the ligands in the equatorial plane. The two $\text{f}\delta$ orbitals in this manifold cannot be used for σ bonding to the equatorial ligands leaving only a smaller five-orbital $\text{d}^3\{\text{d}\sigma, \text{d}\delta\}\text{f}^2\{\text{f}\phi\}$ manifold suitable for equatorial σ bonding. Pentagonal bipyramidal complexes of the type AnO_2L_5 , which are known experimentally to be favored for monodentate L ligands, use this five-orbital submanifold most effectively to form σ bonds to all five equatorial ligands as indicated by the angular overlap parameters calculated for these orbitals. Hexagonal bipyramidal complexes of the type AnO_2L_6 are less favorable as formation of σ bonds to all six equatorial ligands (L) must necessarily either disturb the orbitals required for the linear $\text{O} \equiv \text{An} \equiv \text{O}$ substructure or use high-energy actinide p orbitals. Angular overlap calculations on octahedral complexes of the type AnO_2L_4 show very uneven overlap between the orbitals in the $\text{d}^3\{\text{d}\sigma, \text{d}\delta\}\text{f}^2\{\text{f}\phi\}$ manifold with the four equatorial ligands. Thus the angular overlap model supports the experimental observation that the most favorable actinyl coordination geometry is the pentagonal bipyramidal AnO_2L_5 in the absence of ligands with special properties.

Keywords: Angular overlap; Actinyl complexes; Calculations; Actinide coordination complexes; Uranium

1. Introduction

An important feature of the coordination chemistry of uranium as well as the neighboring actinides, namely neptunium, plutonium and americium, is the ability to form strong covalent bonds in one dimension and weaker bonds in the other two dimensions, leading to what might be called anisotropic coordination chemistry. More specifically, the anisotropy of the coordination chemistry of these actinides arises from the inertness

†This paper is dedicated to the late Prof. Arthur Martell in view of his seminal contributions to coordination chemistry.

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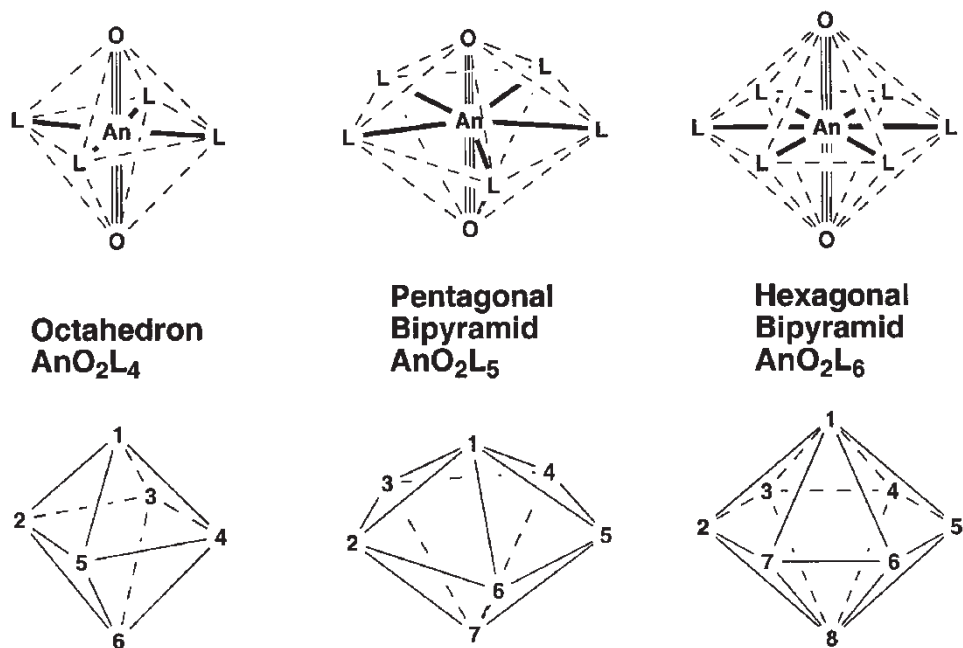


Figure 1. Coordination polyhedra for actinyl complexes and the numbering of their vertices used in tables 2 to 4.

of the linear actinyl unit $O\equiv An\equiv O$ ($An = U, Np, Pu, Am$) [1,2], with short, strong axial actinide–oxygen triple bonds (~ 1.7 to 1.8 \AA for UO_2^{2+}) towards substitution as compared with the equatorial ligands [3,4]. Thus this actinyl unit is preserved during most chemical transformations of these actinides in the +5 and +6 oxidation states. For this reason the coordination chemistry of the actinyl ions is restricted to the equatorial plane. Possible coordination polyhedra of the actinyl ions (including the axial oxygen atoms as coordination sites) are the octahedron, pentagonal bipyramid and hexagonal bipyramid (figure 1) [4,5]. Among these three possibilities the pentagonal bipyramid appears to be preferred with simple monodentate ligands [6–9] including the hydrated uranyl ion $UO_2(H_2O)_5^{2+}$ [10]. Octahedral coordination occurs with π -donor ligands such as the chloride ion [11] in $UO_2Cl_4^{2-}$ and the hydroxide ion [12,13] in $UO_2(OH)_5^{2-}$. Hexagonal bipyramidal coordination is found with small bite bidentate ligands such as nitrate, carbonate [14–16], acetate [1] and oxalate [18].

This article uses the angular overlap model to study the coordination polyhedra found in actinyl complexes (figure 1). The angular overlap model was first suggested by Jørgensen *et al.* [19] and has been applied extensively for the study of d-block transition metal coordination chemistry. Subsequent publication of the formulas for the overlap parameters for f orbitals [20] has allowed this approach to be extended to coordination polyhedra found in complexes of the f-block metals [21]. However, the results of Warren [21] do not consider the special case of actinyl complexes, where strong axial bonding limits the coordination chemistry to the equatorial plane.

2. Calculations

The calculations in this paper assume that the 6p orbitals of the actinides are too high in energy for chemical bonding so that a 13-orbital sd^5f^7 manifold is used [22–24]. As the D_{nh} point groups of the actinyl coordination polyhedra ($n = 4, 5, 6$) have no irreducible representations of higher degeneracies than 2, the general rather than the cubic set of f orbitals is used [25–27]. These f orbitals as well as the d orbitals in actinyl complexes can be partitioned into subsets according to their symmetries relative to the $O\equiv An\equiv O$ axis, considered as the z axis (table 1 and figure 2). Thus the orbitals of σ , π , δ and ϕ symmetries correspond to orbitals with 0, 1, 2 and 3 nodes, respectively, in the xy plane.

The calculations of angular overlap parameters (tables 2–4) were performed using angular parameters obtained from the paper by Smith and Clack [20].

3. Results and discussion

The short strong axial metal–oxygen bonds in actinyl complexes are considered to be $M\equiv O$ triple bonds with one σ component and two orthogonal π components. The relevant orbital submanifold of the sd^5f^7 actinide orbital manifold for the $O\equiv An\equiv O$ substructure is $sd^2\{d\pi\}f^3\{f\sigma, f\pi\}$ leaving a seven-orbital submanifold $d^3\{d\sigma, d\delta\}f^4\{f\delta, f\phi\}$ for σ and π bonding to the equatorial ligands. Furthermore, the two $f\delta$ orbitals in this manifold cannot be used for σ bonding to the equatorial ligands leaving only a smaller five-orbital $d^3\{d\sigma, d\delta\}f^2\{f\phi\}$ submanifold suitable for equatorial σ bonding

Table 1. Axial symmetry of d and f orbitals in actinyl complexes.

σ -bonding (zero axial nodes)	$d\sigma: z^2$	$f\sigma: z^3$
π -bonding (one axial node)	$d\pi: xz, yz$	$f\pi: xz^2, yz^2$
δ -bonding (two axial nodes)	$d\delta: xy, x^2-y^2$	$f\delta: xyz, z(x^2-y^2)$
ϕ -bonding (three axial nodes)	$d\phi: \text{none}$	$f\phi: x(x^2-3y^2), y(3x^2-y^2)$

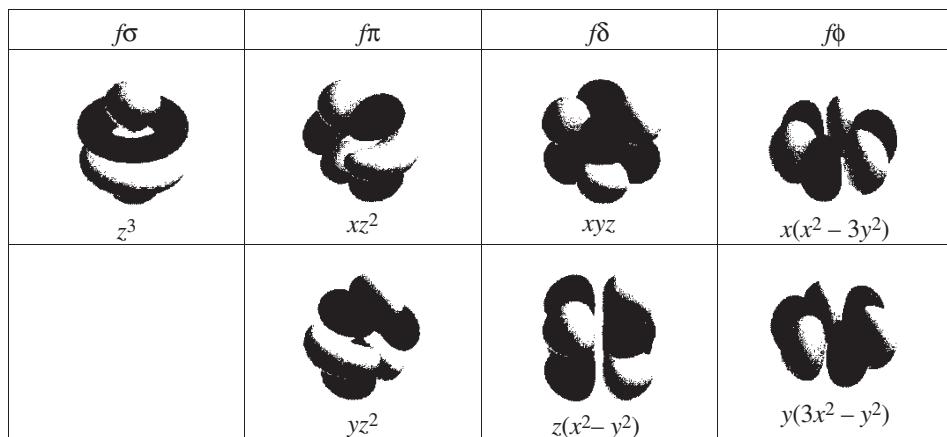


Figure 2. The seven f orbitals discussed in this paper (the z axis is the vertical axis in the plane of the paper).

Table 2. Angular scaling factors for octahedral actinyl complexes, AnO₂L₄.

	z^2	x^2-y^2	xz	yz	xy	z^3	xz^2	yz^2	xyz	$z(x^2-y^2)$	$x(x^2-3y^2)$	$y(3x^2-y^2)$
1σ	1	0	0	0	0	1	0	0	0	0	0	0
1π _⊥	0	0	1	1	0	0	1	1	0	0	0	0
1π _∥	0	0	0	0	0	0	0	0	0	0	0	0
2σ	1/4	3/4	0	0	0	0	3/8	0	0	0	5/8	0
2π _⊥	0	0	0	0	1	0	0	1/16	0	0	0	15/16
2π _∥	0	0	1	0	0	3/8	0	0	0	5/8	0	0
3σ	1/4	3/4	0	0	0	0	0	3/8	0	0	0	5/8
3π _⊥	0	0	0	0	1	0	1/16	0	0	0	15/16	0
3π _∥	0	0	0	1	0	3/8	0	0	0	5/8	0	0
4σ	1/4	3/4	0	0	0	0	3/8	0	0	0	5/8	0
4π _⊥	0	0	0	0	1	0	0	1/16	0	0	0	15/16
4π _∥	0	0	1	0	0	3/8	0	0	0	5/8	0	0
5σ	1/4	3/4	0	0	0	0	0	3/8	0	0	0	5/8
5π _⊥	0	0	0	0	1	0	1/16	0	0	0	15/16	0
5π _∥	0	0	0	1	0	3/8	0	0	0	5/8	0	0
6σ	1	0	0	0	0	1	0	0	0	0	0	0
6π _⊥	0	0	1	1	0	0	1	1	0	0	0	0
6π _∥	0	0	0	0	0	0	0	0	0	0	0	0

Table 3. Angular scaling factors for pentagonal bipyramidal actinyl complexes, AnO₂L₅.

	z^2	x^2-y^2	xz	yz	xy	z^3	xz^2	yz^2	xyz	$z(x^2-y^2)$	$x(x^2-3y^2)$	$y(3x^2-y^2)$
1σ	1	0	0	0	0	1	0	0	0	0	0	0
1π _⊥	0	0	1	1	0	0	1	1	0	0	0	0
1π _∥	0	0	0	0	0	0	0	0	0	0	0	0
2σ	0.250	0.750	0	0	0	0	0.375	0	0	0	0.625	0
2π _⊥	0	0	0	0	1	0	0	0.062	0	0	0	0.938
2π _∥	0	0	1	0	0	0.375	0	0	0	0.625	0	0
3σ	0.250	0.500	0	0	0.250	0	0.036	0.339	0	0	0.409	0.216
3π _⊥	0	0.346	0	0	0.654	0	0.056	0.006	0	0	0.324	0.614
3π _∥	0	0	0.095	0.905	0	0.375	0	0	0.216	0.409	0	0
4σ	0.250	0.071	0	0	0.679	0	0.245	0.130	0	0	0.060	0.566
4π _⊥	0	0.905	0	0	0.095	0	0.021	0.041	0	0	0.848	0.090
4π _∥	0	0	0.654	0.346	0	0.375	0	0	0.566	0.059	0	0
5σ	0.250	0.071	0	0	0.679	0	0.245	0.130	0	0	0.060	0.566
5π _⊥	0	0.905	0	0	0.095	0	0.021	0.041	0	0	0.848	0.090
5π _∥	0	0	0.654	0.346	0	0.375	0	0	0.566	0.059	0	0
6σ	0.250	0.500	0	0	0.250	0	0.036	0.339	0	0	0.409	0.216
6π _⊥	0	0.346	0	0	0.654	0	0.056	0.006	0	0	0.324	0.614
6π _∥	0	0	0.095	0.905	0	0.375	0	0	0.216	0.409	0	0
7σ	1	0	0	0	0	1	0	0	0	0	0	0
7π _⊥	0	0	1	1	0	0	1	1	0	0	0	0
7π _∥	0	0	0	0	0	0	0	0	0	0	0	0

without conflicting with the π bonding in the O \equiv An \equiv O substructure. Note that the $f\sigma$ orbital is used in preference to the $d\sigma$ orbital for σ bonding in the O \equiv An \equiv O substructure because of the inversion center dictating an equal number of *gerade* and *ungerade* orbitals [28,29].

The participation of the individual orbitals in the $d^3\{d\sigma,d\delta\}f^2\{f\phi\}$ submanifold for σ bonding to the equatorial ligands in the three types of AnO₂L_{*n*} complexes ($n=4, 5, 6$) is summarized in table 5 in terms of the sums of the angular overlap parameters. Table 5 also includes similar information on the two $f\pi$ orbitals, which

Table 4. Angular scaling factors for hexagonal bipyramidal complexes, AnO₂L₆.

	z^2	x^2-y^2	xz	yz	xy	z^3	xz^2	yz^2	xyz	$z(x^2-y^2)$	$x(x^2-3y^2)$	$y(3x^2-y^2)$
1σ	1	0	0	0	0	1	0	0	0	0	0	0
1π _⊥	0	0	1	1	0	0	1	1	0	0	0	0
1π _∥	0	0	0	0	0	0	0	0	0	0	0	0
2σ	1/4	3/4	0	0	0	0	3/8	0	0	0	5/8	0
2π _⊥	0	0	0	0	1	0	0	1/16	0	0	0	15/16
2π _∥	0	0	1	0	0	3/8	0	0	0	5/8	0	0
3σ	1/4	3/16	0	0	9/16	0	3/32	9/32	0	0	5/8	0
3π _⊥	0	3/4	0	0	1/4	0	3/64	1/64	0	0	0	15/16
3π _∥	0	0	1/4	3/4	0	3/8	0	0	15/32	5/32	0	0
4σ	1/4	3/16	0	0	9/16	0	3/32	9/32	0	0	5/8	0
4π _⊥	0	3/4	0	0	1/4	0	3/64	1/64	0	0	0	15/16
4π _∥	0	0	1/4	3/4	0	3/8	0	0	15/32	5/32	0	0
5σ	1/4	3/4	0	0	0	0	3/8	0	0	0	5/8	0
5π _⊥	0	0	0	0	1	0	0	1/16	0	0	0	15/16
5π _∥	0	0	1	0	0	3/8	0	0	0	5/8	0	0
6σ	1/4	3/16	0	0	9/16	0	3/32	9/32	0	0	5/8	0
6π _⊥	0	3/4	0	0	1/4	0	3/64	1/64	0	0	0	15/16
6π _∥	0	0	1/4	3/4	0	3/8	0	0	15/32	5/32	0	0
7σ	1/4	3/16	0	0	9/16	0	3/32	9/32	0	0	5/8	0
7π _⊥	0	3/4	0	0	1/4	0	3/64	1/64	0	0	0	15/16
7π _∥	0	0	1/4	3/4	0	3/8	0	0	15/32	5/32	0	0
8σ	1	0	0	0	0	1	0	0	0	0	0	0
8π _⊥	0	0	1	1	0	0	1	1	0	0	0	0
8π _∥	0	0	0	0	0	0	0	0	0	0	0	0

Table 5. Sums of angular overlap parameters from tables 2 to 4 for the actinide coordination geometries AnO₂L_n ($n = 4, 5, 6$) depicted in figure 1.

	AnO ₂ L ₄ ($n = 4$)	AnO ₂ L ₅ ($n = 5$)	AnO ₂ L ₆ ($n = 6$)
<i>Orbitals available for σ bonding to L</i>			
z^2 (dσ)	1	1.250	1.5
x^2-y^2 (dδ)	3	1.892	2.25
xy (dδ)	0	1.858	2.25
$x(x^2-3y^2)$ (fφ)	1.25	1.563	3.75
$y(3x^2-y^2)$ (fφ)	1.25	1.564	0
\sum_A	6.5	8.128	9.75
\sum_A/n	1.625	1.625	1.625
<i>Orbitals prevented from σ bonding to L by being preempted for O≡An≡O π bonding</i>			
xz^2 (fπ)	0.75	0.937	1.125
yz^2 (fπ)	0.75	0.938	1.125
\sum_B	1.5	1.875	2.250
\sum_B/n	0.375	0.375	0.375

have the correct symmetry to participate in σ bonding to the equatorial ligands but are preempted by the requirements of the π bonds in the O≡M≡O unit. In table 5 the sums of the angular overlap parameters for σ bonding in all of the equatorial positions are first considered for each type of orbital in the five-orbital $d^3\{d\sigma, d\delta\}f^2\{f\phi\}$ submanifold. The sums of these parameters for all five orbital types for each AnO₂L_n coordination geometry (\sum_A) are then computed. The average value of these sums per equatorial ligand (\sum_A/n) is 1.625 (= 13/8) for each of the three AnO₂L_n coordination geometries. The deviation of \sum_A/n from 2.000 arises from the overlap parameters of the two fπ orbitals, which have the correct symmetry for σ bonding to the equatorial ligands

but are not available as they are preempted for the π components of the actinyl $\text{An}\equiv\text{O}$ triple bonds. A similar calculation of the sums of the angular overlap parameters of these two $f\pi$ orbitals \sum_{B} followed by taking their averages leads to a consistent value of 0.375 for \sum_{B}/n for any of the three coordination geometries. Note that $\sum_{\text{A}} + \sum_{\text{B}} = 1.625 + 0.375 = 2.000$ as expected.

Analysis of the angular overlap parameters for the atomic orbitals in the five-orbital $d^3\{d\sigma, d\delta\}f^2\{f\phi\}$ submanifold provides an excellent rationalization for the prevalence of pentagonal bipyramidal structures in actinyl coordination chemistry. First, there are only five orbitals of the 13-orbital sd^5f^7 manifold available for σ bonding of the central actinide to the equatorial ligands so hexagonal bipyramidal geometry with actinide–ligand covalent bonding is not possible without either using higher energy actinide p orbitals or some of the orbitals required for the axial σ and π bonding in the $\text{O}\equiv\text{An}\equiv\text{O}$ unit. Second, the sums of the overlap parameters of all five orbitals in the $d^3\{d\sigma, d\delta\}f^2\{f\phi\}$ submanifold are seen to be equal within $\pm 25\%$ (table 5), which means that each orbital can participate effectively in the bonding of the central actinide to the five ligands of the equatorial pentagon in AnO_2L_5 complexes. Such is not the case for octahedral AnO_2L_4 complexes in which one of the orbitals in the $d^3\{d\sigma, d\delta\}f^2\{f\phi\}$ submanifold, namely the xy orbital, is not able to overlap with any of the equatorial ligands and the overlap of the x^2-y^2 orbital with the equatorial ligands is seen to have at least $2(1/2)$ times the overlap of any other orbital in the $d^3\{d\sigma, d\delta\}f^2\{f\phi\}$ submanifold. However, the xy orbital, which is not available for equatorial σ bonding, is seen in table 2 to be very suitable for equatorial π bonding with a similar \sum_{π} sum of 4. This may account for the fact that octahedral actinyl geometry is found with π donor ligands in anions such as $\text{UO}_2\text{Cl}_4^{2-}$ and $\text{UO}_2(\text{OH})_4^{2-}$ noted above.

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