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Bonding in Tris(η^5-cyclopentadienyl) Actinide Complexes. 2. On the Ground Electronic Configurations of "Base-Free" Cp_3An Complexes (An = Th, Pa, U, Np, Pu)[1]

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Abstract: Quasi-relativistic $X\alpha$–SW calculations have been carried out on the "base-free" tris(η^5-cyclopentadienyl) actinide complexes Cp_3Th (**1**) and Cp_3U (**2**). Unlike the actinide complexes Cp_3AnL (L = neutral two-electron donor), for which all of the An 6d orbitals are used as electron acceptors, **1** and **2** both contain a low-lying $6d_{z^2}$ orbital that competes with the 5f orbitals for the metal-based electrons. It is predicted that **1** will have a $6d^1$ electron configuration, which agrees with recent EPR experiments by Edelstein, Lappert, et al. It is also predicted that, unlike Cp_3UL complexes, which have a $5f^3$ electron configuration, **2** might have a $6d^15f^2$ ground configuration. Results are also presented for Cp_3Pa, Cp_3Np, and Cp_3Pu.

We have been investigating the electronic structure of organoactinide complexes that contain three cyclopentadienyl (or modified cyclopentadienyl) ligands. The reasons for these studies are manifold: (1) This is perhaps the most common coordination found among organoactinide complexes;[3] the first organoactinide complex synthesized, Cp_3UCl,[4] was of this type, and compounds are known for actinide elements ranging from Th[5] to Cf.[6,7] (2) The presence of three η^5-Cp ligands would force quantization of the actinide 5f and 6d elements about a threefold axis, and this may produce different electronic structural effects than quantization about a two- or fourfold axis (as found in Cp_2AnX_2 or Cp_4An derivatives). (3) For the more common actinide elements Th and U, it has been possible to synthesize (and interconvert) tris(cyclopentadienyl) complexes with the actinide in either the +3 or +4 oxidation state, thus allowing the influence of individual electrons to be assessed and portending a rich redox chemistry for these organometallics. (4) Among the known U(III) complexes of this class is Cp'_3UCO[8] ($Cp' = \eta^5\text{-}Me_3SiC_5H_4$), the first example of a discrete actinide–carbonyl complex (the bonding in which we have discussed previously).[1] (5) While there is a plethora of actinide complexes containing three η^5-Cp ligands, there are only two bona fide examples for the transition elements, viz., $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$[9] and $(\eta^5\text{-}C_5H_5)_3Zr(\mu\text{-}H\text{-}AlEt_3)$,[10] and thus this class provides a nice contrast of organoactinide and organotransition element chemistry.

A thesis that we have developed throughout our molecular orbital studies of organoactinide electronic structure concerns the dichotomy of roles played by the actinide (An) 5f and 6d orbitals.[1,11,12] We have found that the An 6d orbitals dominate the bonding of ligands to the actinide atom; i.e., they serve as the acceptors of charge from donor ligands. The 5f orbitals act as primary acceptor orbitals only if, by symmetry, the 6d orbitals cannot, as is the case for the a_2 ligand group orbital that arises from the π_2 MOs of three η^5-Cp ligands.[12] The principal function of the 5f orbitals is to act as a reservoir for metal-based electrons; thus, in Cp_3UCO, a model of the known complex Cp'_3UCO, we found that the three metal-based electrons of this formally U(III) complex reside in nearly pure U 5f orbitals and that these are capable of back-bonding to the CO ligand.[1] We have found this description to be valid for all U(III) Cp_3UL and U(IV) Cp_3UX complexes that we have investigated.[1,12]

In the case of tris(η^5-cyclopentadienyl)uranium(III) chemistry, the majority of known complexes contain a fourth basic, generally neutral ligand L lying on the threefold axis of the Cp_3U unit.[6a] Crystallographic studies on these Cp_3UL complexes show them to be structurally isomorphic to U(IV) derivatives Cp_3UX in that the Cp ligands are in a C_{3v} pyramidal arrangement with the L–U–Cp(centroid) angles > 90°.[13] The lone pair of ligand L denotes into an axially oriented acceptor orbital of a_1 symmetry that is predominantly U $6d_{z^2}$ in character. This acceptor orbital is, for geometric (i.e., overlap) reasons, ineffective for acceptance

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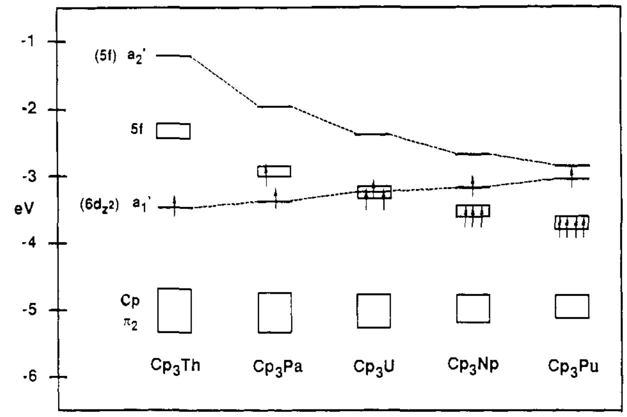

Figure 1. Metal-based orbital energies for the $5f^{n-1}6d^1$ electron configurations of planar Cp_3An (An = Th, Pa, U, Np, Pu) complexes.

from the Cp ligands and is thus completely available to the ligand L.[12]

It has also been possible to isolate "base-free" Cp_3An complexes, and two of these, Cp''_3Th ($\mathbf{1}''$; $Cp'' = \eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3$)[5a] and Cp'_3U ($\mathbf{2}'$),[14] have recently been structurally characterized. Both $\mathbf{1}''$ and $\mathbf{2}'$ exhibit planar, pseudo-D_{3h} structures with respect to the metal–Cp(centroid) vectors. Under the planar geometry, the axial acceptor orbital (now of a_1' symmetry under D_{3h}) is still unable to interact effectively with the Cp ligands. It therefore is not destabilized by metal–ligand bonding and, if low enough in energy, could compete with the 5f orbitals for the metal-localized electrons. Here we report spin-restricted and spin-unrestricted quasi-relativistic $X\alpha$–SW MO calculations[15] on Cp_3Th (**1**) and Cp_3U (**2**), in both planar and pyramidal geomtries, that provide support for the occupation of the a_1' 6d-based orbital, leading to a different metal electron configuration in **1** and **2** relative to Cp_3AnL complexes. For comparison to the calculational results on **1** and **2**, we also report calculations on Cp_3Pa, Cp_3Np, and Cp_3Pu, the first electronic structure calculations on cyclopentadienyl derivatives of these elements.

Results and Discussion

The metal-based valence MOs of **1** in the planar configuration are depicted in Figure 1. Under pseudo-D_{3h} symmetry, the Th 6d orbitals span the $a_1' + e' + e''$ representations, and only the latter two are strongly destabilized by interaction with the Cp rings. It is seen that the a_1' orbital, the Th portion of which is 89% $6d_{z^2}$ and 11% 7s, is the lowest metal-based orbital, being ca. 1 eV lower than the lowest 5f orbital (e''). As shown in Figure 1, this results in a formal $6d^1$ electron configuration for **1**. We have also converged the calculation with the metal-based electron occupying the e'' orbital, leading to a $5f^1$ configuration. This still results in the a_1' orbital being lower than the 5f orbital; unlike Hartree–Fock methods, unoccupied orbitals in the $X\alpha$ method are not artificially destabilized.[15] As shown in Figure 2a, the a_1' orbital of planar **1** is a diffuse Th $6d_{z^2}$ orbital directed along the threefold axis of the molecule.

An experimental determination of the ground electron configuration of $\mathbf{1}''$ by EPR spectroscopy has recently been reported by Edelstein, Lappert, et al.[16] They find a $6d^1$ configuration, in agreement with the results presented here. Interestingly, they assume a separation of 20 000 cm^{-1} between the $^2A_1'$ ground state and the $^2E''$ excited state; the $X\alpha$ statistical total energies of the two configurations of **1**, which must be considered of questionable reliability, indicate a separation of ca. 11 000 cm^{-1} (spin-restricted) or 9500 cm^{-1} (spin-unrestricted), lending credence to their assumption.

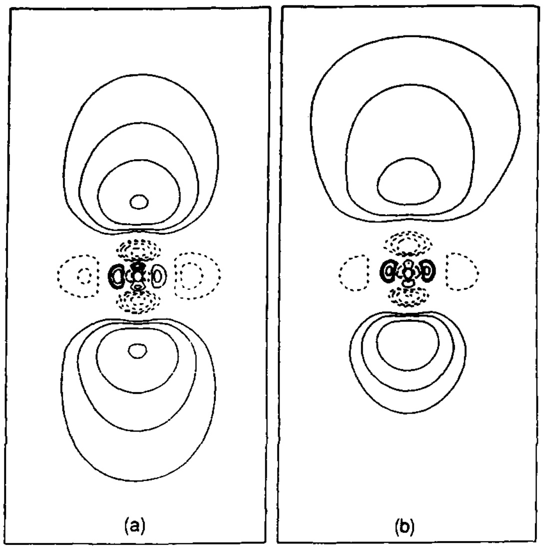

Figure 2. Contour plots of (a) the a_1' orbital of planar **1** and (b) the a_1 orbital of pyramidal **1**. The plot areas are ±4.23 Å in *z* (the threefold axis) and ±2.12 Å in *x* relative to the Th atom. Contour values are ±0.040, ±0.060, ±0.090, and ±0.135.

In pyramidal **1**, there is further hybridization of this orbital (a_1 under C_{3v}) such that it is directed toward the vacant coordination site of the molecule (Figure 2b). It would thus be an ideal acceptor orbital for the lone pair of a fourth ligand. This principally 6d a_1 orbital of pyramidal **1** is also found to be lower than the 5f orbitals, but coordination of a fourth ligand destabilizes this orbital to well above the 5f orbitals. We would therefore expect Th(III) Cp_3ThL complexes to exhibit a $5f^1$ electron configuration. Some Cp_3ThL complexes have been reported for L = THF or CNC_6H_{11},[5b] but, to our knowledge, there have been no studies of their ground electronic properties.

This somewhat surprising result in the case of **1** led us to investigate the ground electron configuration of Cp_3M compounds of the later actinides. The electronic structures of Cp_3Th through Cp_3Pu in the $6d^15f^{n-1}$ (*n* = number of metal-based electrons in the +3 oxidation state) electron configurations are depicted in Figure 1. Consistent with earlier experimental results,[17] the 5f orbitals are lowered in energy as one proceeds from Th to Pu. This leads to a situation in which the 5f block of orbitals will "pass through" the 6d-based a_1' orbital and, as a result, reside below the a_1' orbital.[18] As was the case in **1**, the a_1' orbital of the hypothetical Cp_3Pa molecule still resides below the 5f block of orbitals, leading to the prediction of a $6d^15f^1$ ground electron configuration of this as-yet-unknown molecule. For the transuranium compounds (cf. Cp_3Np and Cp_3Pu in Figure 1) the a_1' orbital resides above the 5f block of orbitals and leads to the prediction of the $6d^05f^n$ ground electron configuration. In the case of Cp_3U there seems to be a unique situation that warrants further discussion.

Cp_3UL complexes are invariably found to have a $5f^3$ ground configuration. In both the planar and pyramidal geometries of base-free complex **2**, however, we find the participation of the $6d_{z^2}$ orbital to be important; the removal of the fourth ligand removes the destabilization of this orbital, making it essentially isoenergetic with the 5f orbitals (Figure 1). For planar **2**, we find the $6d^15f^2$ ($a_1'^1e''^2$) configuration to be approximately equal in energy to the $5f^3$ configuration, with a difference in the spin-unrestricted $X\alpha$

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Table I. Sphere Radii (Å) and α Parameters for Cp_3M

	atom	sphere radius	α
	C	0.8984	0.75928
	H	0.6783	0.77725
M = Th	outer sphere	4.0788	0.75929
	Th	1.7112	0.69200
M = Pa	outer sphere	4.0700	0.75844
	Pa	1.6933	0.69200
M = U	outer sphere	4.0701	0.75762
	U	1.6879	0.69200
M = Np	outer sphere	4.0701	0.75682
	Np	1.6830	0.69200
M = Pu	outer sphere	4.0701	0.75604
	Pu	1.6659	0.69200

statistical total energies of only 100 cm^{-1}! While we are reluctant to believe the quantitative validity of the $X\alpha$ total energies,[19] we do believe the trends to be properly indicated and therefore suggest that a different ground electronic configuration might exist for **2** than for Cp_3UL complexes. The possibility of a $6d^15f^2$ ground configuration for **2** appears to be at odds with a previous calculational study on the U(IV) complex $\mathbf{2}^+$, which places the $6d_{z^2}$ orbital ca. 4 eV above the 5f orbitals.[23] We look forward to the experimental determination of the ground configuration of **2**.

Computational Details

Quasi-relativistic $X\alpha$–SW calculations were carried out in analogy to those previously reported.[1] Structural parameters for **1** and **2** were taken from the crystal structures of **1″** and **2′**.[5a,14] The structural parameters for Cp_3Pa, Cp_3Np, and Cp_3Pu were set equal to those of **2**. Both the planar and pyramidal Cp_3M (M = Th, Pa, U, Np, Pu) calculations were performed under C_{3v} symmetry. The basis functions included all spherical harmonics through $l = 4$ on the outer sphere, $l = 3$ on M, $l = 1$ on C, and $l = 0$ on H. The starting potentials for each molecule were superpositions of neutral atomic Herman–Skillman potentials of the constituent atoms. The atomic sphere radii were chosen as 89.0% of the atomic number radii. The sphere radii and the α parameters are summarized in Table I. The calculations were first converged spin-restricted, and the converged spin-restricted potential was used as a starting potential for the spin-unrestricted calculations. Spin-restricted and spin-unrestricted total energies were calculated according to Slater's formalism.[15]

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[19] There have undeniably been difficulties in using the $X\alpha$–SW total energy to calculate equilibrium geometries and potential surfaces, in largest part because of the problems associated with sphere radius selection.[20] In the results reported here, we are keeping the molecular geometries and sphere radii fixed; only the orbital occupations are changed. We believe that this will achieve a reasonable separation of "geometric" and "electronic" contributions to the total energy, and we have more confidence in the latter than the former. As support for the application of $X\alpha$–SW total energies in these types of systems, we note that Edelstein et al.[21] estimate the splitting between the $5f^1$ and $6d^1$ configurations of $PaCl_6^{2-}$ to be ca. 22 000 cm^{-1}. The difference in spin-unrestricted $X\alpha$–SW statistical total energies is calculated to be 28 000 cm^{-1}, with the $5f^1$ configuration correctly predicted as the ground configuration.[22]

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Bonding in Tris(η^5-cyclopentadienyl) Actinide Complexes. 3. Interaction of π-Neutral, π-Acidic, and π-Basic Ligands with (η^5-C_5H_5)$_3$U[1]

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Abstract: A qualitative treatment of the bonding in Cp_3M (Cp = η^5-C_5H_5) compounds under C_{3v} symmetry reveals that the Cp_3^{3-} ligand field contains a high-lying a_2 orbital which is restricted by symmetry to interact only with metals that contain f orbitals. Quantitative investigation of the electronic structure of "$5f^3$" Cp_3U via $X\alpha$-SW molecular orbital calculations with quasi-relativistic corrections reveals that the Cp ligands donate electron density primarily into the U 6d orbitals while the three principally metal-based valence electrons are housed in the 5f orbitals. Electronic structure calculations of Cl_3U show that although Cl can be considered isolobal with Cp, it is a poorer donor ligand. Calculations of Cp_3U bonded to a fourth ligand L (L = H, CO, NO, OH) indicate that the σ-bonding framework is essentially the same for π-neutral (H), π-acidic (CO, NO), or π-basic (OH) ligands: Electron density is donated from the σ orbital of the fourth ligand into a uranium orbital that is primarily $6d_{z^2}$ in character with minor contributions from the $5f_{z^3}$ orbital, the $7p_z$ orbital, and the 7s orbital. In the π-bonding framework, the U 5f orbitals are responsible for back-donation into the π^* orbitals of CO and NO, while acceptance of electron density from the π orbitals of OH involves the U 6d orbitals and, to a lesser extent, the U 5f orbitals. The bonding scheme of Cp_3UNO suggests that this molecule may prove to be a rather unusual example of a linear NO^- ligand.

Organoactinide chemistry has received considerable attention in the last two decades.[3] As was the case for organotransition-metal chemistry, the growth of this field has been intimately coupled with the use of the π-coordinating cyclopentadienyl (Cp)

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