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An MO Study on Structures and Reactivity of Organoactinides Based on the Extended Hückel Method: Actinide Bis(cyclopentadienyl) Complexes*

KAZUYUKI TATSUMI† and AKIRA NAKAMURA

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Abstract

This contribution describes a brief summary of extended Hückel MO characterization of bis(cyclopentadienyl) (Cp) complexes of actinides. Some $Cp^*_2AnL_2$ molecules (An = actinide; Cp* = pentamethylcyclopentadienyl; L = η^2-pyrazolate, η^2-acyl, etc.) assume 20-electron structures violating the EAN rule. Our calculations show the observed geometries to be in fact electronically most stable, in contrast to the d-metal analogs which exhibit a strong tendency to obey the EAN rule. Characteristic features of the Cp_2An fragment orbitals are emphasized. The electronic origins of the unusual alkyl deformation in $Cp^*_2Th(CH_2CMe_3)_2$ are also ascribable to the unique bonding ability of the actinide fragment.

Introduction

We have witnessed, in the past decade, that syntheses of a variety of new organo-actinide and -lanthanide complexes have progressed from dream to reality; many had been thought impossible to make. Mostly owing to efforts by synthetic chemists, modern f-transition metal chemistry has grown to become a part of, indeed a good part of, inorganic and organometallic chemistry [1]. We may admit that theory in this field is still incomplete in its predictive power, and it is a challenge. The challenge is thus to use modern quantum mechanics and to achieve some degree of understanding of the electronic structures and reactivity of actinide and lanthanide molecules.

We have applied the extended Hückel MO method to this field and have found the theoretical implications quite useful despite the approximate nature of the calculations [2]. In this contribution we briefly view how this simple method has been used to elucidate electronic factors determining properties of thorium and uranium complexes containing the Cp_2An (Cp = cyclopentadienyl; An = actinide) fragment, and particular emphasis is put on its ability to bind ligands yielding high total coordination numbers.

Theoretical Background

It is generally recognized that relativistic effects are hardly negligible for very heavy elements in assessing their chemical properties. For instance, about 10% of the well-known lanthanide contraction, where the observed ionic radius drops from 1.061 Å for La to 0.848 Å for Lu, comes from the relativistic contribution [3a]. The energies arising from the relativistic terms are comparable to chemical bond energies for elements in the range gold–bismuth, and such terms become even more important in the case of the actinides.

Excellent accounts of relativistic quantum chemistry [3] have been reported and a detailed review with an extensive bibliography [4] is also available. From comparisons of relativistic and non-relativistic wave functions for atoms, the three main effects have been derived in an explicit manner: (i) the relativistic contraction; (ii) the spin–orbit splitting; and (iii) the relativistic self-consistent expansion. The effect (i) originates from the mass–velocity term in the Dirac equation and is applied mostly to s and $p_{1/2}$ subshells. Then an indirect consequence of the mass increase, $m = m_0/\sqrt{1-(v/c)^2}$, is effect (iii). That is, the d and f electrons, having high angular momenta, expand spacially due to screening of the nuclear attraction by the contracted s and p orbitals. These two effects also influence orbital energy levels, lowering s and p orbital levels and raising d and f levels. On the other hand, effect (iii) leads to energy splitting between a pair of *j* values for a p, d or f orbital.

For parametrization within a framework of the extended Hückel method, we determine or choose suitable atomic wave functions and valence-state ionization energies (H_{ii}). The valence orbital basis sets for actinides include 7s, 7p, 6d, 6p and 5f, in

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†Author to whom correspondence should be addressed.

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which 6p is regarded as a semi-core subshell. Complete tables of accurate self-consistent field calculations based on the relativistic Dirac–Fock equation are given by Desclaux [5], which yield orbital energies, radii and other expectation values of $1/r, r^2$, etc. for ground states of entire atoms. They are convenient and quite helpful in determining appropriate actinide parameters for extended Hückel calculations.

Our choice of atomic radial functions of the actinide 6d and 5f orbitals are of Slater-type with double-ζ quality, while the other valence-orbital functions are of single-ζ type. The orbital exponents were estimated from Desclaux's numerical wave functions: the double-ζ parameters for 6d and 5f were computed by fitting them to $R_{\max}$ (radius of maximum radial density), $\langle r \rangle$, $\langle r^2 \rangle$ of $6d_{5/2}$, $6d_{3/2}$, $5f_{7/2}$, $5f_{5/2}$ and the single-ζ parameters for 7s and 7p to $R_{\max}$ of $7s_{1/2}$, and those for 6p to $R_{\max}$ of $6p_{1/2}$. The relativistic 6d and 5f functions were then transformed to 'quasi-relativistic' orbitals by taking weighted averages of each multiplet.

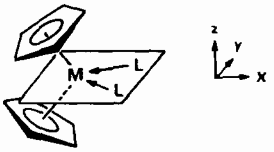
The valence state ionization energies or the diagonal terms (H_{ii}) of extended Hückel matrices were also taken from the orbital energies of the Desclaux's functions. Occasionally the H_{ii} values were estimated by the standard charge consistent approach, in that the diagonal elements were approximated as a parabolic function of the atomic charge in terms of the Mulliken population analysis. The parameters for the charge-iterative calculations were determined on the basis of the Dirac–Slater relativistic atomic calculations for appropriate electronic configurations [6, 2j]. The quasi-relativistic extended Hückel parameters for Th and U have been tabulated in our previous papers [2f, j], and those for Pa, Np, Pu and Am are also available [7]. The off-diagonal elements H_{ij} are calculated by a weighted Wolfsberg–Helmholtz formula which has been successfully used for calculations on d-transition metal complexes, and we apply the standard K value of 1.75 to actinide systems as well.

Thus the relativistic effects (i) and (iii), together with the energy level shifts associated with the orbital size changes, within actinide atoms remain implicitly intact in our 'quasi-relativistic' extended Hückel method. Not included in our formalism is the spin–orbit splitting (effect (ii)), but this effect would not be indispensable as far as ground state properties such as geometries and reactivity are concerned, particularly for systems having f^0 electronic configurations. Also not included is the difference in size between two multiplets of p, d and f orbitals, where a subshell with a larger j value (e.g., $f_{7/2}$) expands more than that with a smaller j value (e.g., $f_{5/2}$). When these effects are to be examined, one may use the 'relativistically parametrized extended Hückel (REX) method' developed by Lohr Jr. and Pyykkö [8]. A series of parameter sets for actinides and for lanthanides has also been reported [9].

Sample Problems

To see how the approximate MO method works, let us discuss some specific problems. Among a respectable number of organo-actinide complexes, one ubiquitous structure is that consisting of the bent bis(η^5-cyclopentadienyl)metal fragment. While the actual molecules often carry pentamethylcyclopentadienyl ligands (Cp*), they are replaced by non-substituted cyclopentadienyl (Cp) for our theoretical analysis.

In most Cp_2ML_n complexes with d- and f-transition metals, coordination of ligands L occurs in the equatorial xy plane (**1**). The number of ligands (n) varies depending on the choice of the central metal (M). For d-transition metal Cp_2ML_n complexes, n is determined according to the EAN rule, and thus the total number of electrons around the metal should not exceed 18. But this restriction does not apply to actinide complexes. Examples of 20-electron compounds include $Cp^*{}_2U(\eta^2\text{-pz})_2$ (pz^- = pyrazolate) [10], $Cp_2U(acac)_2$ [11], $Cp^*{}_2An(\eta^2\text{-COR})_2$, $Cp^*{}_2An(\eta^2\text{-CONR}_2)_2$ [12], and $Cp_2U[(O_2C_2{-}CHPCH_3(C_6H_5)_2)Fe_2Cp_2(CO)_2]_2$ [13]. In this electron count, the f-electrons for An = U(IV) are disregarded. Particularly instructive may be the complexes of pz^- and COR^- (and $CONR_2^-$) which can assume in principle either η^1 or η^2 coordination geometry. For η^1 these ligands act as two-electron donors, and for η^2 they are four-electron donors. Then why do they choose the bis-η^2 coordination geometry in the actinide systems despite the fact that the molecules apparently violate the EAN rule?



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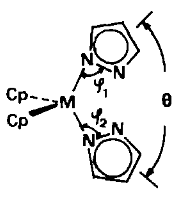
Consider the three pyrazolate complexes, $Cp_2Mo(pz)_2$, $Cp_2Mo(pz)_2^{2+}$ and $Cp_2U(pz)_2$. The first Mo complex may represent a class of bis(cyclopentadienyl) (d-metal) molecules with a d^2 configuration, while the latter dicationic Mo model represents those with a d^0 configuration. We have calculated potential energy surfaces for the molecules as a function of the M–N–N angles φ_1, φ_2 and the pz–M–pz angle θ as defined in **2**. The extended Hückel parameters for Mo and U are taken from previous work, and the results are summarized in Fig. 1.



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In the potential surface of Fig. 1 (top) for $Cp_2Mo(pz)_2$, a minimum comes at $\varphi_1 = \varphi_2 = 128^\circ$ and $\theta = 52.5^\circ$. The optimum mode of pyrazolate coordination is computed thus of the η^1–η^1 type, which satisfies the EAN rule. The 20-electron η^1–η^2 structure (e.g., $\varphi_1 = 125^\circ$, $\varphi_2 = 70.3^\circ$, $\theta = 80^\circ$) was calculated to be 3.1 eV higher in energy, and the 22-electron η^2–η^2 was still much less stable. In going from the d^2 system to the d^0 $Cp_2Mo(pz)_2^{2+}$ complex, the η^1–η^2 structure ($\varphi_1 = 123.8^\circ$, $\varphi_2 = 70.3^\circ$, $\theta = 82.5^\circ$) becomes most stable (Fig. 1 (middle)). Electron deficiency caused by decrease of the d-electron number is reasonably compensated by making one pyrazolate ligand a four-electron donor (η^2), thus satisfying again the EAN rule.

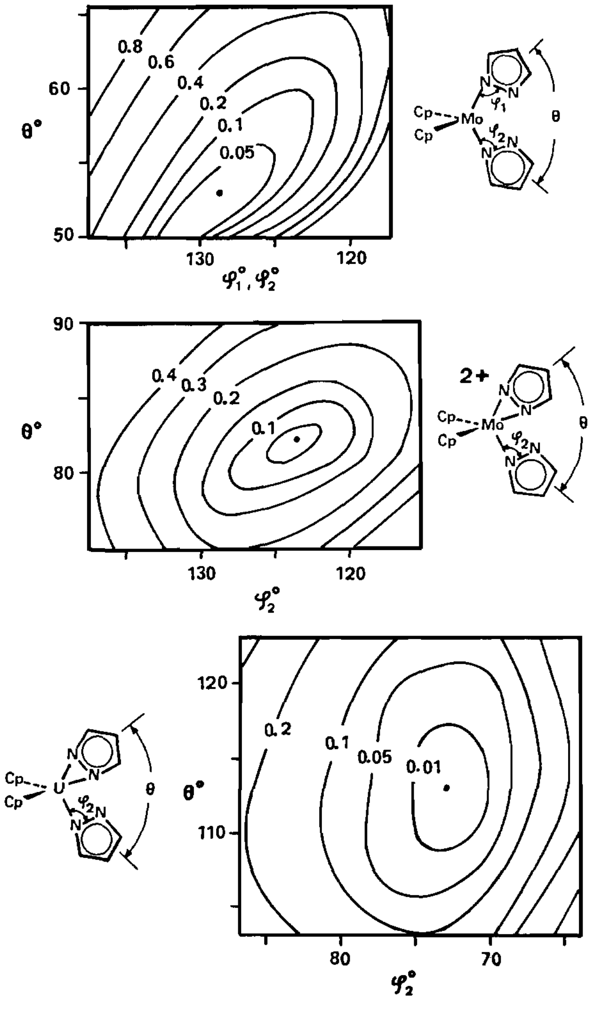


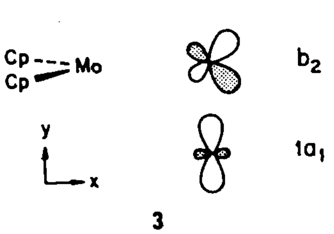
Fig. 1. Potential energy surfaces as a function of φ_1, φ_2, and θ for $Cp_2Mo(pz)_2$ (top), $Cp_2Mo(pz)_2^{2+}$ (middle, $\phi_1 = 70.3^\circ$), and $Cp_2U(pz)_2$ (bottom, $\varphi_1 = 73^\circ$). The points shown by • indicate the energy minima; the contours are marked in electron volts.

Since pyrazolate exhibits a strong tendency to bridge two metal centers, $Cp_2Mo(pz)_2$ is a rare example of η^1-pz on a single metal. Both the Ti and Mn congeners have dinuclear structures, $[Cp_2Ti(pz)]_2$ [14] and $[(OC)_3Mn(1,2\text{-}\eta^2\text{-}pz)_3Mn(CO)_3]^-$ [15]. Notwithstanding, should d^0 and d^2 $Cp_2M(pz)_2$ complexes be made, their structures would be η^1–η^2 and η^1–η^1, respectively, as the calculations indicate.

The uranium complex (and thorium as well) $Cp_2U(pz)_2$ is apparently similar to $Cp_2Mo(pz)_2^{2+}$ in that both have a formal d^0 configuration. However their optimum modes of pz coordination are quite different. As can be seen in Fig. 1 (bottom), our calculations on $Cp_2U(pz)_2$ gave an η^2–η^2 minimum at $\varphi_1 = \varphi_2 = 73^\circ$ and $\theta = 113^\circ$, and the η^1–η^2 geometry is no longer stable, in harmony with the experimental result. It should be noted here that the computed structure is very close to the X-ray derived structure of $Cp^*_2U(pz)_2$ with the angles $\varphi_1 = 75.4^\circ$, $\varphi_2 = 75.1^\circ$ and $\theta = 112.2^\circ$. Perhaps the good agreement shows the validity of the calculation method.

Based on the population analysis, we see all the U–N bonds to be formed properly. The U–N overlap populations are large, being 0.257 for the outside-N and 0.260 for the inside-N. The somewhat larger U–N(inside) overlap population is consistent with the observed trend of U–N lengths in $Cp^*_2U(pz)_2$, where the U–N(inside) bond distances (2.360, 2.363 Å) are slightly shorter than the U–N(outside) distances (2.403, 2.405 Å).

The difference in geometrical choice between $Cp_2Mo(pz)_2(\eta^1$–$\eta^1)$, $Cp_2Mo(pz)_2^{2+}(\eta^1$–$\eta^2)$ and $Cp_2U(pz)_2(\eta^2$–$\eta^2)$ can be explained in terms of frontier orbital interactions between the Cp_2M fragments and bis(pz). For Cp_2Mo, there are three familiar low-lying d and s–p hybrid orbitals in the xy plane (3), and each pyrazolate carries two occupied



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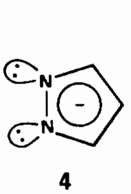
N lone-pair orbitals (**4**). In the case of d^2 Cp_2Mo, the vacant $2a_1$ and b_2 are used for bonding with *two* η^1-pyrazolate N lone-pairs, while the occupied $1a_1$ is left as an innocent metal lone-pair orbital. With two electrons less, Cp_2Mo^{2+} forms bonds with *three* N lone-pairs by use of all the three frontier orbitals (**3**), resulting in the η^1–η^2 structure. Still the Cp_2Mo^{2+} fragment cannot hold bonding with the *fourth* N lone-pair. In other words, the molybdenum 5s, 5p and 4d orbitals are unable to overlap with the (n_-–n_-) symmetry molecular orbital of the η^2–η^2 bis(pz) (**5**).



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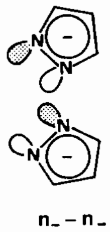

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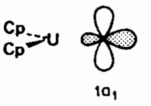
The Cp_2U^{2+} fragment also has the vacant $2a_1$, b_2 and $1a_1$ orbitals similar to **3**. However they are significantly higher in energy and are more diffuse than the Cp_2Mo^{2+} frontier orbitals. The shape of $1a_1$ (**6**) is also different. The orbital lobe pointing in the direction of $+x$ is as large as those in the $\pm y$ direction [2j], in contrast to the nearly pure y^2 character of Cp_2Mo^{2+} $1a_1$. These characteristic features of the Cp_2U^{2+} frontier orbitals aid the U atom, in one way or another, to hold two η^2-pyrazolates in the equatorial girdle. Another important and pictorial factor is the presence of the vacant U f_{yx^2} orbital (**7**). Its nodal property is just right in interacting with the occupied pyrazolate n_-–n_- orbital. Therefore the valence orbitals of Cp_2U allow all the *four* N lone-pair orbitals to participate in bonding in the η^2–η^2 geometry.



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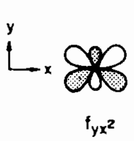

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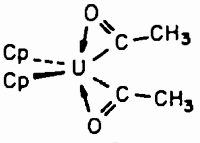
The situation is very similar to the bis(acyl) and the bis(carbamoyl) complexes $Cp_2M(COR)_2$ and $Cp_2M(CONR_2)_2$. We have performed calculations on both the U(IV) and Ti(IV) molecules to find that an η^2–η^2 structure is again favored when M = U (**8**), while the Ti analog opts for an 18-electron η^1–η^2 structure [2g]. The reasoning used for the geometrical contrast between the bis(pyrazolate) complexes of U and Mo can be applied to the acyl and carbamoyl systems as well. Our calculations were also able to give a clue in understanding the unique reactivity of η^2-acyl ligands in the bis(cyclopentadienyl) complexes. More specifically, the electrophilic reactivity of the η^2-acyls was attributed to the presence of a low-lying carbenium-ion-like acceptor orbital [2f].



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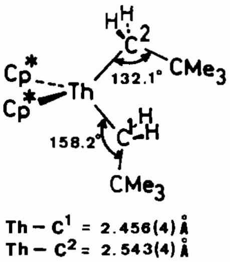
Another interesting example is $Cp^*_2Th(CH_2CMe_3)_2$ (**9**) [16]. According to an accurate neutron diffraction study, it displays an unusual structure deformation in which the Th–C^1–C(alkyl) angle is remarkably obtuse (α = 158.2°). The potential energy curve for the ethyl pivoting in $Cp_2Th(C_2H_5)_2$ was found to be very soft, with a shallow minimum at $\alpha \simeq 160°$ [2j]. The detailed orbital analysis traced the deformation to the characteristic shape and size of the fragment orbitals of $Cp_2Th(C_2H_5)^+$ and, in turn, to those of the Cp_2Th^{2+} frontier orbitals which were analogous to the aforementioned Cp_2U^{2+} orbitals. Despite the deformation, the ethyl group is bound strongly to Th. Actually the computed Th–C overlap population for the distorted ethyl was even slightly larger than that for the other less-distorted ethyl in $Cp_2Th(C_2H_5)_2$, in accord with the observed structure **9**.



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Acknowledgements

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Note Added in Proof

In fact, d^2 $Cp_2Mo(pz)_2$ was found to assume an η^1–η^1 structure with the pz–Mo–pz angle of 83.3(1)°, in accord with our calculations. See, M. A. A. F. DE C. T. Carrondo and A. M. T. S. Domingos, *J. Organomet. Chem.*, *253*, 53 (1983), and see also, M. J. Calhorda and A. R. Dias, *Organomet. Chem.*, *197*, 291 (1980).