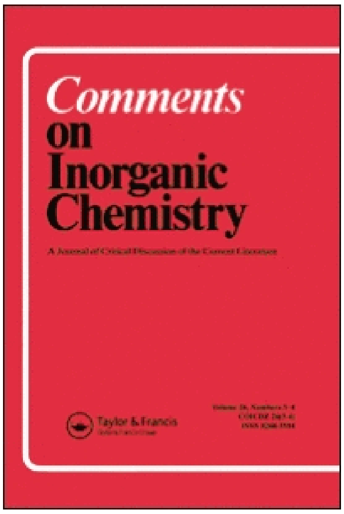

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Covalency in f-Element Organometallic Complexes: Theory and Experiment

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Covalency in f-Element Organometallic Complexes: Theory and Experiment

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The bonding of organo-f-element complexes is examined both by review of theoretical considerations and by examination of experimental methods to determine the extent of covalency. While ligand–metal orbital overlap is important in rigorous descriptions of electronic structure (and therefore in many spectroscopic studies), only in a few cases do covalent contributions significantly perturb the chemical behavior of the compounds.

Key Words: *actinide, lanthanide, bonding, covalency, ionicity, f-orbitals, organometallic, electronic structure*

INTRODUCTION

The characterization of ferrocene as a π-bound cyclopentadienyl complex[1] is generally considered the event that introduced the modern age of transition metal organometallic chemistry. Reports

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of ferrocene were rapidly followed by the preparation of the first organo-f-element complexes that utilized the cyclopentadienyl ligand.[2] The organometallic chemistry of the lanthanide and actinide elements has developed steadily, particularly in the last 20 years, and has been the subject of a number of excellent recent review articles.[3] One notable difference between organometallic complexes of the d- and f-transition elements has been in the level of understanding of the molecular bonding. While the bonding in d-transition metal organometallic compounds has been studied extensively at virtually all levels of experimental sophistication and computational complexity, only recently have researchers begun to examine rigorously the bonding in their f-element analogs, especially with regard to the nature of the metal–ligand bond. Two seemingly disparate views of bonding in organo-f-element chemistry currently persist. Many researchers maintain that, because the descriptive chemistry of these species is indicative of primarily ionic bonding, the complexes should be considered only in this way, with perturbations to point charge interactions being introduced by the inclusion of ion polarization. An alternative view is to discuss the bonding of the molecules in terms of molecular orbitals, with the relatively large charge separation in the bonds resulting from the energetic separation of metal and ligand-based orbitals. A combination of theoretical and experimental evidence is available to assess the ways in which these models differ, and in how they agree.

THEORETICAL STUDIES

Interest in the bonding of organometallic f-element complexes has been in evidence since the first reports of the synthesis of these species. A qualitative discussion of the orbital interactions in $(C_5H_5)_3U^+$ by W. Moffitt was included in the report of the synthesis of $(C_5H_5)_3UCl$ in 1956.[2c] In this discussion, the metal orbitals and the hybrids derived from the ligand valence orbitals were analyzed by symmetry under the point group D_{3h}. The important feature of this discussion was the recognition, even at this early stage, that while some of the ligand orbitals were of the proper symmetry to interact with either metal d- or f-orbitals, other ligand combinations could interact by symmetry only with f-orbitals. This model, although based on overlap of metal and ligand orbitals of like symmetry, allowed the possibility of a high degree of ionic character in the bonding by permitting the variation of a parameter that represented the amount of cyclopentadienyl ring orbital character contributing to the bonding orbitals.

The recognition that actinide and lanthanide f-orbitals possess unique symmetry for interaction with ligand-based orbitals led to the theoretical prediction and subsequent preparation of "sandwich" compounds of the f-elements with the cyclooctatetraene (COT or π-[8]annulene) ligand.[4] The bonding in these highly symmetric compounds has been studied extensively. The earliest molecular orbital treatments made the assumption that the ligand orbitals interacted only with the f-orbitals of appropriate symmetry, and that the metal d-orbitals were too high in energy to interact with the ligands.[5] It was further argued, in analogy to the interaction between the ligand e_{1g} and metal d-orbital interaction in transition metal metallocenes, that the strongest interaction in COT complexes should be between the ligand e_{2u} and the metal f-orbitals (Fig. 1). It was suggested that this interaction should be energetically favorable as well, i.e., the f-orbitals were energetically close to the ligand e_2 orbitals, and would introduce a strong component of covalent bonding to the complexes (Fig. 2). This energetic assumption persisted in other calculations, either in the form of assumed metal valence state ionization potentials in Wolfsberg–Helmholz calculations,[6] or as assumed relative orbital energies in ligand field treatments.[7] The first indications that such assumptions might not produce an accurate picture of the metal–ring bonding resulted from INDO-SCF calculations on $[Ce(COT)_2]^-$.[8] These authors noted that the calculated total energy of the system was very dependent on the degree of metal 5d orbital mixing with the ring orbitals, giving rise to f-d repulsion terms that rivaled in energy the overall calculated ligand–field splitting of the 4f orbitals.

Subsequent relativistic and quasi-relativistic calculations have somewhat amended the description of ring–metal overlap.[9,10] The use of approximations to the full Dirac–Slater treatment leads to the expected lowering of the metal $(n + 1)$s and $(n + 1)$p levels, and the accompanying expansion of the $(n - 1)$f orbitals due to

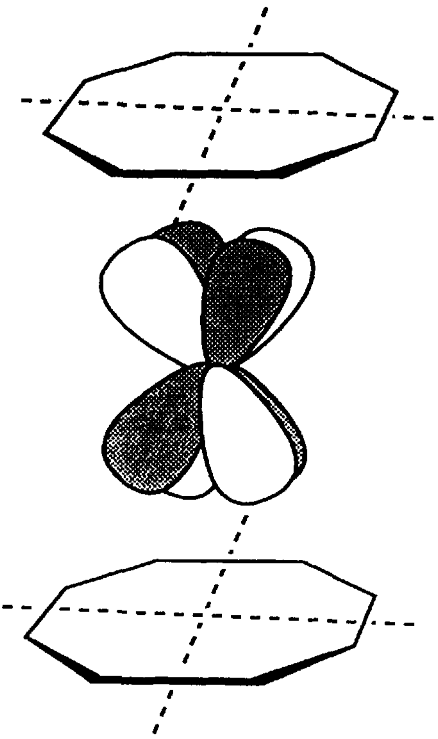


FIGURE 1 Metal–ligand interaction in the e_{2u} molecular orbital of uranocene.

improved shielding of the nuclear charge.[11] In some cases, corrections have also been included (either implicitly or explicity) for the consequences of spin-orbit coupling. Two types of calculations have been used principally to examine the bonding in f-element COT compounds with some form of relativistic compensation. One method is a relativistically parameterized version of extended Hückel theory (REX), which introduces relativistic effects through the use of $|lsjm >$ quantized atomic orbital basis sets.[9] The other is a SCF-Xα scattered-wave (Xα-SW) MO method with the inclusion of quasi-relativistic corrections within a one-electron framework for mass–velocity and Darwin terms.[10] Both studies assumed an idealized D_{8h} molecule with geometrical parameters based on the known

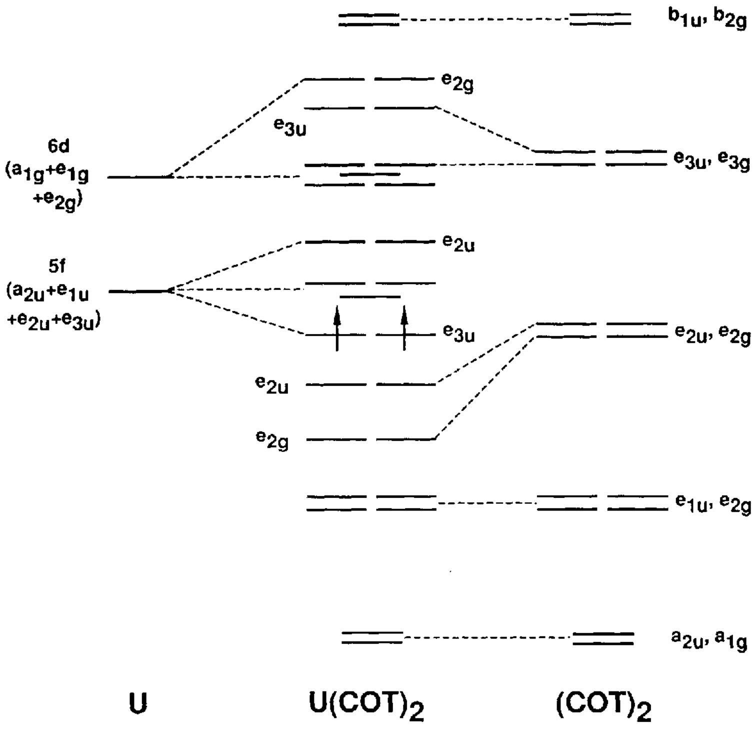


FIGURE 2 Qualitative MO diagram of uranocene.

structure of uranocene, and a U basis set consisting of the 7s, 7p, 6d, and 5f atomic orbitals. The results of these calculations are qualitatively similar (Fig. 3), in that they both predict that two electrons will reside in essentially metal-based f-orbitals (giving rise to the observed paramagnetism of the complex). The two molecular orbitals below the HOMO (e_{2u} and e_{2g}) are derived from the ligand π-set. The predicted energies of these orbitals are in reasonable accord with experimentally derived values.[12] The two models differ in their estimation of the metal orbital contribution to these "ligand derived" HOMO's, however. The REX calculation predicts average metal orbital contributions to the e_{2u} set of 11.6% (by symmetry only mixing with f-orbitals), and 10.7% to

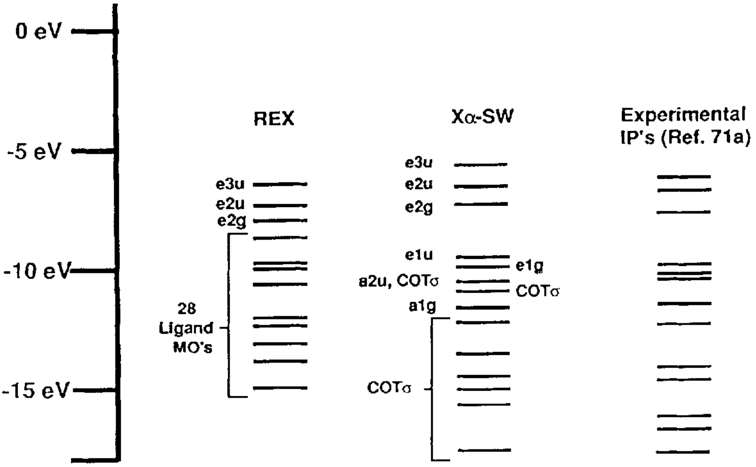


FIGURE 3 Comparison of the REX and Xα-SW orbital energies with the experimental ionization potentials of uranocene.

the e_{2g} set (mixing with d-orbitals), while the Xα-SW calculation predicts metal orbital contributions of 33% and 20% to the e_{2u} and e_{2g} MO's, respectively. Based on these differences, very different conclusions are drawn. The authors of the REX calculation calculated an atomic charge of + 4.10 on the uranium in uranocene, and classed the bonding as ionic.[9] It was later suggested, however, that the parameterization in this model led to exaggerated ionicity; properties such as the e_{2u}-e_{2g} splitting and atomic charge derived from the total Xα population of the metal sphere indicated increasing f-orbital covalency.[10] A recent *ab initio* calculation on uranocene including spin-orbit CI also indicates a high degree of covalency, primarily involving the U 6d orbitals in the formation of the U-COT bonds.[13] This same conclusion has been reached on the basis of relativistic Hartree–Fock–Slater calculations.[14] Although there are still disagreements in the theoretical treatments of f-element COT complexes over what justifies the term "covalence," it is generally agreed that the metal d-orbitals are just as important in a description of metal–ring interations as the f-orbitals.

Despite the fact that an overwhelming proportion of f-element organometallic chemistry is based upon the cyclopentadienyl ligand system, only recently have these systems been treated theoretically. To date, very few calculations have been performed on lanthanide complexes in this class. Extended Hückel calculations have been performed on Cp_2Ln complexes.[15] In these calculations, the Ln 4f-orbitals were ignored, and the molecules were treated as d^0 complexes in order to examine the interactions of metal fragment orbitals with ligands. A subsequent localized INDO study concluded that there was significant covalency in the complex $(C_5H_5)_2LuCl(thf)$, based on the calculated charge on the Lu atom, and on the calculated metal–ligand bond orders.[16] Perhaps the most detailed examination of bonding in lanthanide cyclopentadienyl complexes has been the quasi-relativistic Xα-SW calculations performed on the model compounds $(C_5H_5)_2Ln$ (Ln = Eu, Yb), in conjunction with PES studies on the monomeric C_5Me_5 (Cp*) analogs.[17] In these studies, geometrical parameters were taken from gas-phase electron diffraction data, and the calculations were performed for both D_{5d} and C_{2v} geometries. Only very small charge localization of the ligand-derived orbitals was observed inside the metal sphere, and these authors concluded that the compounds were best described by an ionic bonding model. This proposal was supported by the extremely small ligand–field splitting of the 4f orbitals. It is interesting to note that for both the Xα-SW and EH calculations, the equilibrium geometry of a Cp_2Ln fragment was proposed to be D_{5d} (or D_{5h}), whereas the observed geometry in the solid state and gas phase is C_{2v} (i.e., the Cp rings are "bent"). This will be discussed further in the section on Experimental Studies.

More extensive studies have been carried out on cyclopentadienyl complexes of the actinides, particularly uranium. One of the primary motivations in examining these complexes has been to study more directly the comparison between the bonding of transition metal complexes and their f-metal structural analogs (there are no $M(COT)_2$ complexes in the transition metal series for direct comparison with uranocene). The quasi-relativistic extended Hückel method has been employed to study the bonding in actinide complexes, often for the purpose of examining the potential surfaces for reaction pathways.[18] In general, these calculations suggest that metal f-orbitals hybridize only slightly with d-orbitals to form the frontier fragment MO's, but that in certain cases f-orbital participation may be enhanced. For example, there are indications in calculations on $Cp_2MX(COR)$ and $Cp_2M(COR)$ complexes that actinide 5f orbitals participate in the bonding through overlap with the η^2-acyl ligands, and may help stabilize high-electron counts relative to analogous d-transition metal complexes.[18b] It has also been suggested that actinide hybridized orbitals with substantial f-character may overlap with unsaturated ligand orbitals in butanediyl complexes.[18c] A recent series of EH calculations on a number of Cp_3U complexes with N and O donor ligands has been reported by Cramer *et al.*[18d] These studies suggest that the Cp ligands induce a large splitting of the U 6d orbitals; further splitting is caused by donor ligands with π-symmetry orbitals available for overlap with the metal orbitals. The authors report a large overlap population (0.703) between U and N in the complex Cp_3UNPH_3, the MO diagram of which is shown in Fig. 4. The σ component of the overlap population is slightly larger than its π complement. This is usually taken as an indication of covalent bonding. Curiously, the charge on U is quite high (+ 3.20), which would seem indicative of ionic bonding. This illustrates the difficulty in interpreting theoretical results in terms of the labels "ionic" and "covalent."

Systems such as those above have also been studied by using the quasi-relativistic $X\alpha$-SW molecular orbital method.[19] By utilzing idealized geometrical parameters obtained from crystallographic studies, and assumed sphere radii and α values, orbital energies have been calculated along with their orbital "parentage." Some of the first studies utilizing this method were comparisons of the bonding in UCl_4, Cp_2UX_2, and UCp_4.[20] The results of these calculations are summarized in Fig. 5. Several factors were considered important in evaluating the molecular orbital results. It was observed that, for the most part, the 5f manifold of uranium is perturbed very little in complex formation, consistent with the results of the EH calculations.[20] The destabilization and energetic spread of this manifold, however, was taken as an indication of the strength of the interaction of the ligands with the metal center. Substitution of chloride ligands by cyclopentadienyl groups leads to an increase in the energy and the splitting of the f manifold,

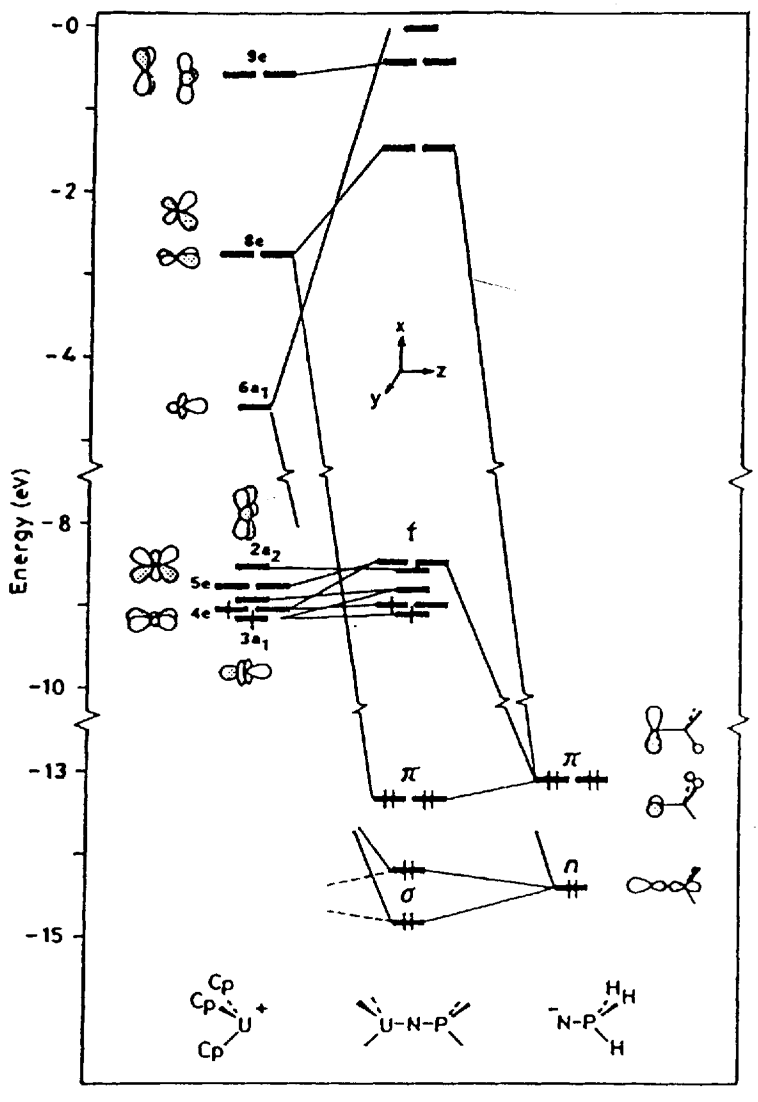


FIGURE 4 Molecular orbital diagram of Cp_3UNPH_3 (Ref. 18d).

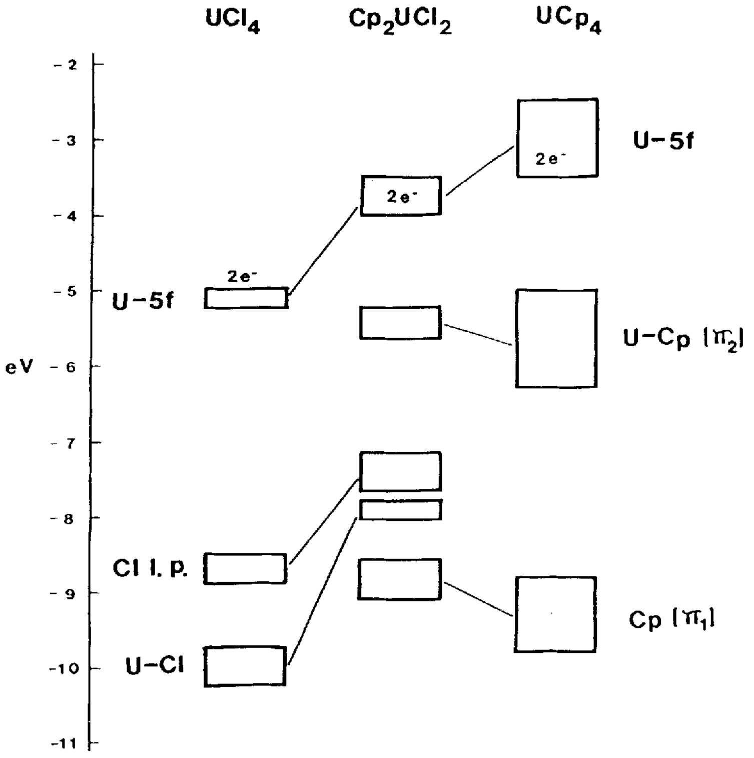


FIGURE 5 Comparison of the orbital energies in Cp_4U, Cp_2UCl_2, UCl_4 (Ref. 20b).

indicating that the Cp ligand is a stronger donor group than the halide. Examination of the splitting of the molecular orbitals formally derived from the ligand π_2 orbitals was then used as a criterion to judge which metal orbitals (6d or 5f) were most stabilized by electron density donation from the ligands. The greater stabilization of the e π_2 orbitals (capable of containing only 6d-orbital character by symmetry) relative to the t_1 π_2 orbitals (capable only of containing 5f-orbital character) was interpreted as implying a stronger ligand–metal d-orbital interaction. This conclusion was reached in spite of the fact that the e set was calculated to contain less uranium orbital character (17% 6d) than the t_1 set (23% 5f). As would be expected, the calculated results for Cp_2UCl_2 suggested the orbital energetics of this complex were intermediate between those for UCp_4 and UCl_4 (Fig. 5), although the cyclopentadienyl ligands seemed to dominate the position of the 5f manifold, owing to their electron-rich nature. Ionization potentials calculated for UCp_4 with Slater's transition-state formalism[21] were in fair agreement with those from experimental PES data.[22]

While these calculations performed on cyclopentadienyl complexes of uranium indicated ligand–metal orbital mixing, it appeared that the strongest ligand-to-metal σ-donation was into metal 6d orbitals, leaving the 5f orbitals relatively undisturbed as the HOMO's of the molecules. Subsequent Xα-SW calculations that have been performed on Cp_3UL complexes seem to indicate that the f orbitals may be capable of interacting with π-symmetry ligand orbitals.[23] An examination of the electronic structure of Cp_3UCO (as a model for the recently reported $(C_5H_4SiMe_3)_3UCO$[24]) suggests that the CO lone pair interacts with a metal 6d orbital to form a bonding interaction of approximately 27% metal character. The highest occupied orbitals on the Cp_3U fragment, the 5f orbitals, are of the proper symmetry to interact with the π^* orbitals of CO to form a bonding orbital which contains approximately 14% ligand orbital character, but virtually no contributions from the metal 6d orbitals (Fig. 6). By contrast, when a π-donor ligand is bound to Cp_3U, the ligand donates predominantly into the U 6d orbitals, just as in the case for σ-donation.[23c]

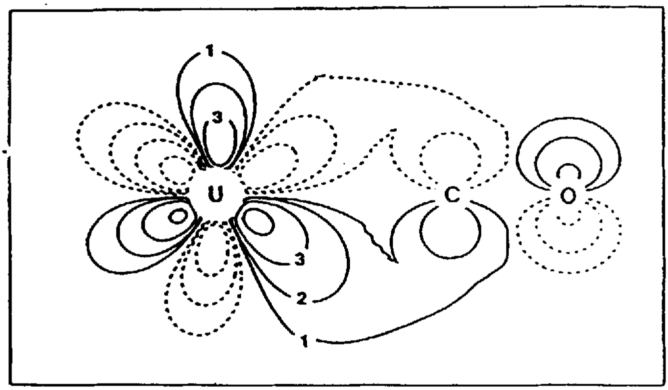
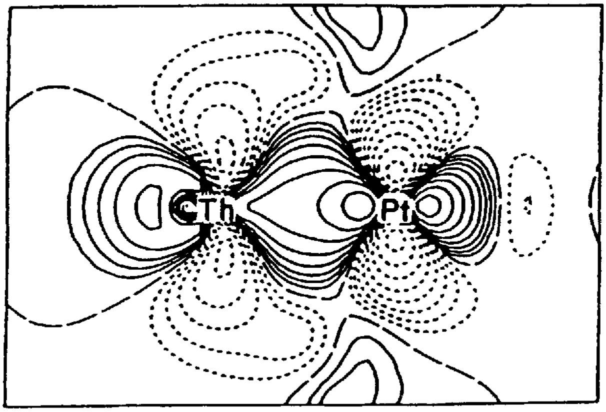


FIGURE 6 HOMO of $(C_5H_5)_3UCO$ (Ref. 23a).

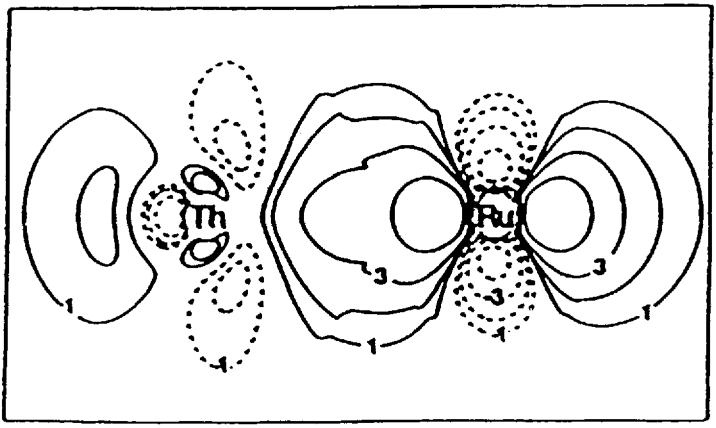
One other class of organometallic actinide complexes bears mentioning in any discussion of covalent bonding: complexes possessing metal–metal bonds. There are few reported examples of complexes in which transition metal–actinide bonds are claimed, but calculations have been performed on two examples of such species. Extended Hückel[25a] calculations on $Cp_2Th(\mu\text{-}PH_2)_2Ni(CO)_2$ suggest a donor–acceptor relationship between Ni and Th. Preliminary reports of *ab initio*[25b] calculations on $Cl_2Th(\mu\text{-}PH_2)_2Pt(P_3)$ (as a model for the complex $Cp^*_2Th(\mu\text{-}PPh_2)_2Pt(PMe_3)$) support the idea of a Th-Pt bond, and quasi-relativistic Xα-SW calculations[26] on $Cp_2(I)Th\text{-}RuCp(CO)_2$ (as a model for $Cp^*_2(I)Th\text{-}RuCp(CO)_2$[27]) also suggest the presence of a metal–metal bond. The common feature in these calculations is a metal–metal bonding HOMO which is derived from a transition metal nd orbital with a small admixture of actinide 6d orbital character. Thus, the bonding interactions in these complexes can best be described as dative transition metal-to-actinide weak electron pair donation, as shown in Fig. 7.

The renewed interest in theoretical examination of the electronic structure of organo-f-element complexes in the past decade has served to correct early biases derived from qualitative descriptions of the $M(COT)_2$ class of compounds. It is now clear, at least in the case of thorium and uranium, that the metal 6d orbitals dominate the bonding with ligands as compared to the 5f orbitals. The latter orbitals house any metal-based electrons that remain, and are of the proper symmetry to interact with π-acid ligands. We have called this the "FEUDAL" description of the bonding in organothorium and -uranium complexes (*"f's essentially unaffected; d's accommodate ligands"*). Recent calculational studies suggest that the importance of the actinide 5f orbitals in interacting with the ligands should increase for organometallics of the transplutonium elements.[28]

It should be clear from the above discussion that the question of covalency in organo-f-element complexes is not an easily answered one. The most important parameter in determining covalency in metal–ligand bonds is the amount of metal character incorporated into ligand-based orbitals (and vice versa). While calculated values of this participation vary widely from calculation to calculation, it is clear that the amount of covalency in organoactinide complexes is higher than that in organolanthanide com-



(a)



(b)

FIGURE 7 Metal–metal interactions in (a) $Cl_2Th(\mu\text{-}PH_2)_2Pt(PH_3)_2$ (Ref. 25b) and (b) $Cp_2(I)Th\text{-}RuCp(CO)_2$ (Ref. 26).

plexes, and lower than that in transition metal complexes. The question remains: "Is the covalent contribution to the bonding in organo-f-element complexes sufficient to affect the expected chemistry of the complexes?" This question is best addressed in the laboratory.

EXPERIMENTAL STUDIES

For as long as theoretical chemists have studied the bonding in organo-f-element complexes, experimentalists have attempted to infer similar information from the chemical and spectroscopic properties of these compounds. Some of the first reports of the syntheses of actinide cyclopentadienyl compounds included qualitative assessments of the bonding based on observations of chemical reactivity.[2] Reaction with $FeCl_2$ to produce ferrocene, with water or other acidic media to produce free cyclopentadiene, or with maleic anhydride to produce the Diels–Alder addition product, was taken as a sign of ionic bonding in a compound. It was determined by early workers that, while the cyclopentadienides of scandium, yttrium and the lanthanides reacted readily in this manner,[2a,b] $(C_5H_5)_3UCl$ did not react with ferrous chloride or ketones, and decomposed relatively slowly in water.[2c] This was taken as proof of "homopolar" or covalent bonding in the case of the actinide complex, i.e., the stability was assumed to be thermodynamic rather than kinetic in origin. The subsequent report of the relative stability of bis(cyclooctatetraene) actinide complexes toward hydrolysis,[4b] in conjunction with theoretical descriptions of bonding, has prompted many experimental endeavors to search for evidence of covalent perturbations to an ionic model for organo-f-element complexes. In contrast to theoretically derived descriptions of electronic structure, only rarely have attempts been made to quantify covalent contributions as based on experimental results.

STRUCTURAL RESULTS

One of the principal experimental arguments for ionic bonding in organo-f-element complexes is based on structural evidence.[29] One model that has proved generally useful in examining structural parameters is rooted in the premise that any given metal–ligand bond length can be predicted if the oxidation state (and hence the ionic radius) of the metal is known, assuming a common set of ionic radii for the same ligand in a series of complexes. The set of ionic radii determined by Shannon[30] has commonly been used in

TABLE I

U-C(Cp) bond lengths for selected U(IV) complexes

Complex	C. N.*	M-C(Cp), Avg. (Å)	Ref.
$U(C_5H_5)_4$	12	2.82	31
$(C_5H_5)_3U(NCS)(MeCN)$	11	2.76	32
$(C_5H_5)_3U(n\text{-}Bu)$	10	2.73	33
$(C_5H_4Me)UCl_2(thf)_2$	8	2.72	34

*C.N. = effective coordination number.

discussions of actinide and lanthanide complexes. A correction must be made to the ionic radius of the metal ion for the effects of interligand repulsions; the larger the effective coordination number of the complex, the larger the ionic radius (the coordination number of the metal ion is defined as the number of electron pairs involved in the ligand–metal interactions). The effect is clearly demonstrated in a comparison of bond distances for a given metal in different coordination spheres (Table I). Any contributions by covalent bonding should lead to an additional shortening of the metal–ligand bond length. Other structural phenomena support the idea of ionic bonding. One common feature in the structures of homoleptic lanthanide cyclopentadienyl complexes is the variability of the hapticity of the ligand ring. This allows the metal ion to maximize contacts with neighboring ligands. This behavior is attributed to the ionic character of the compounds, in that it is also observed in alkali metal and alkaline earth cyclopentadienyl complexes.[35] Another structural feature that has been explained by an ionic bonding model is the commonly observed out-of-plane bending of the methyl groups away from the metal ion in lanthanide complexes of methyl-substituted cyclopentadienyl ligands. This has been interpreted as a mechanism to localize negative charge on the side of the ring facing the metal ion,[36a,b] in contrast to the more "covalent" cyclopentadienyl complexes of the transition met-

TABLE II

Uranium complexes with short M-L distances

Compound	M-C(N)	Ref.
$(C_5H_5)_3UCHP(Me)_2(C_6H_5)$	2.29(3) Å	37a
$(C_5H_5)_3UNC(Me)CHP(Ph)_2Me$	2.06(1) Å	37b
$(MeC_5H_4)_3UNPh$	2.019(6) Å	38a
$(C_5H_5)_3UNPPh_3$	2.07(2) Å	18d
$[N(SiMe_3)_2]_3UNSiMe_3$	1.91(2) Å	38b
$[N(SiMe_3)_2]_3U(F)(NSiMe_3)$	1.85(2) Å	39
$[N(SiMe_3)_2]_3U(F)(NPh)$	1.979(8) Å	39

als, in which the hydrogen atoms on the ring bend toward the metal.[36c]

The early success in prediction of metal–ligand distances based on this model could be interpreted as an indication that there was little or no covalent contribution to the bonding in f-element complexes. This success was based, however, on a relatively narrow selection of ligands and metal oxidation states, *viz.* cyclopentadienyl, halide, and alkyl complexes of trivalent lanthanides and tetravalent actinides. While little structural evidence has emerged to contradict this model in the lanthanide series, several recent reports of actinide complexes that display unusually short metal–ligand bond distances have appeared. Several of these complexes are listed in Table II.

In some cases, the short (relative to M-NR_2 or M-CH_2R distances) M-N and M-C bond lengths have been attributed to metal–ligand multiple bonding, a tacit assumption of significant covalent contribution to the bonding scheme, as discussed above. It is worth noting, however, that an ionic bonding model would also predict a shorter metal–ligand bond distance for a ligand such as an imido group. If considered as a dianion NR^{2-}, the sp hybridized group is expected to have a smaller effective radius than an sp^2-hybridized

NR_2^- ligand; additionally, the Coulombic attraction between the metal and the more highly charged negative ligand should be greater, leading to a shorter bond.

As an actinide is oxidized, the radial extent of the 5f orbitals decreases and their energy is lowered. Thus, they become less available for overlap with ligand orbitals. Therefore, the most prominent effects of f-orbital covalency in organoactinide complexes should be displayed by complexes in the lower oxidation states. A recent comparison of M-Cp and M-L distances for a series of Lewis base adducts of tris(cyclopentadienyl)uranium complexes and trivalent lanthanide analogues indicates that U(III) can act as a base towards π-accepting ligands (e.g., phosphines, phosphites, and isocyanides), displaying U-L distances shortened significantly with respect to the analogous cerium complexes.[40]

Although invoking multiple bonding might help to explain many anomalous structural features of actinide complexes, there are also a few cases where orbital theory has been unable to provide explanations for structural trends. One example is the molecular geometry of low-coordinate f-element compounds such as the tris[bis(trimethylsilyl)amido] and tris[bis(trimethylsilyl)methyl] complexes of the lanthanides and actinides, as well as the bis-Cp* complexes of the divalent lanthanides Eu, Sm, and Yb. The amido and alkyl complexes display a pyramidal geometry,[41] and the Cp* complexes are bent in both the solid state and gas phase.[42] While orbital calculations for these molecules indicate that the potential surface for bending is quite shallow, no rationale for a bent geometry can be found in either extended Hückel or quasi-relativistic SCF-Xα-SW calculations.[15,17] A qualitative explanation for the geometry of these molecules can be found in the polarizable ion model.[43] This model states that the total electrostatic energy of an ionic molecule is determined not only by the charge–charge interactions, but also by charge–dipole interactions. For a polarizable cation surrounded by relatively non-polarizable anions, the dipole moment induced at the cation by lowering the symmetry of the surrounding anions (as by bending the molecule) will interact favorably with the anions, offsetting anion–anion repulsions for small bending angles (Fig. 8). This model has been successfully employed in the calculation of equilibrium geometries of alkaline earth dihalides,[44] and in the prediction of trends in the structures and vibrational frequencies for f-element di- and trihalides.[45]

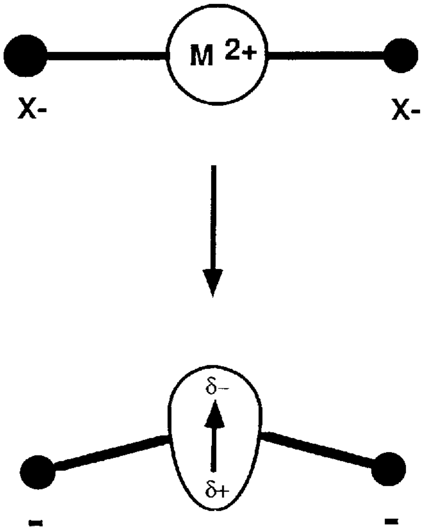


FIGURE 8 Schematic representation of the polarizable ion model.

ELECTRONIC SPECTROSCOPY AND MAGNETIC PROPERTIES

One of the most direct measures of the interaction of ligand-based orbitals with the d and f valence orbitals of lanthanides and actinides is electronic spectroscopy. For the lanthanide elements, the contracted nature of the 4f orbitals ensures that they will be well shielded by the 5s and 5p levels, and not susceptible to perturbations by the ligand sphere. Crystal field splittings are small relative to the spin-orbit coupling, and therefore the magnetic moments of lanthanide ions can be approximated rather well by the Russell–Saunders coupling scheme.[46] For organometallic complexes, covalent contributions to bonding would be expected to appear in the form of enhanced ligand–field splittings and lowered magnetic moments. Experimentally determined magnetic moments for organolanthanide complexes, however, are usually very close to the free ion values,[47] implying that these molecules are still predominantly ionic.

More subtle effects can be inferred from the absorption spectra of lanthanide ions. Again, because of the contracted nature of the 4f orbitals, there is little vibronic coupling to perturb the symmetry, and as a result, the f-f transitions are narrow and very weak in intensity. The effecs of covalency in the bonding would be manifested as a shifting of the position of these bands, perhaps accompanied by an enhancement of intensity. Small perturbations were indeed observed in the earliest organolanthanide complexes.[48] It is interesting to note that the first discussions of this effect described the perturbation in terms of a nephelauxetic or "cloud-expanding" effect in which polarization of the electrons of the lanthanide effects a reduction in interelectron repulsions, and hence a reduction in the separation of the J-levels derived from the f-orbitals.[49]

More exacting analyses have been performed, fitting observed optical spectra to an energy diagram calculated from the Hamiltonian corrected for the effects of electrostatic and spin-orbit interactions, as well as for configuration interaction.[50] While the derived crystal field splittings in base adducts of the tris(cyclopentadienyl) lanthanide compounds are larger than for the free trivalent ions doped into $LaCl_3$, the observed reductions in the values of the Slater parameters and the spin-orbit coupling constants (suggested to provide a measure of covalency[51]) are small, indicating that the compounds are still predominantly ionic.

Although covalency in organolanthanides may not manifest itself in a perturbation of the 4f orbitals, there remains the possibility that the 5d orbitals interact with the appropriate ligand orbitals. One way to probe this is to examine the energy of luminescent transitions from excited states with $4f^{n-1}5d^1$ configurations. Cerium(III) has a lowest excited state with a $4f^05d^1$ configuration.[52] Recent reports of luminescence spectra[53] on a variety of Ce(III) complexes have suggested that there is an increase in covalency of the cerium–ligand bonds in the order L = halide < akyl < Cp < COT, Cp*.

In the actinide series, the increased importance of the spin-orbit correction term to the parametric free ion Hamiltonian complicates the simple L-S coupling scheme. The larger radial extent of the actinide 5f orbitals relative to the lanthanide 4f orbitals allows for greater overlap with ligand orbitals than in the lanthanides, making crystal field effects more important as well. The larger splitting of the J states due to the electrostatic field of the ligands causes the magnetic moments of actinide ions to be somewhat lower than would be predicted by Russel–Saunders coupling. The introduction of an external magnetic field will cause an additional Zeeman splitting in these levels.

Few attempts have been made to derive quantitative magnetic moments for organoactinide complexes, usually due to their relatively low symmetries. One case that has been extensively studied, however, is the bis(cyclooctatetraene) complexes of U, Np, and Pu. The first predictions of the magnetic moment were based on a weak crystal field model,[54] a simple L-S coupling model was assumed, and any deviation of the moment from this value was fitted using an empirically derived orbital reduction factor, described as a measure of the covalency of the molecule. Further study, however, was prompted by the discovery that uranocene does not display simple Curie–Weiss behavior, but rather displays temperature-independent susceptibility below ca. 10 K (this has been generally attributed to a low temperature lowering of the molecular symmetry due to the monoclinic cell).[55] Nonrelativistic molecular orbital calculations[56] were more successful in reproducing the measured moment from 10–80 K by using an effective crystalline field potential to derive the ordering of the one-electron metal-based orbitals. The splittings were then used to evaluate the crystal field parameters. These calculations seemed to indicate a substantial reduction of the charge on the uranium, but it was pointed out that the high value assumed for the 5f valence state ionization potential could cause an overestimation of the covalence in the bonding.

The optical spectra of organoactinide complexes are similarly complicated by the magnitude of the spin-orbit and crystal field splittings. In general the f-f transitions are more intense and broader than in the corresponding lanthanide complexes, and their position is more sensitive to ligand environment; this can often make them more difficult to assign unambiguously. Laporte allowed f-d transitions are lower in energy than in the lanthanide series, and so are more commonly observed. In order to examine rigorously the bonding in organoactinide complexes, it has been necessary to perform analyses as described earlier for the lanthanides, in which observed optical spectra were fit to parameters to correct for electron–electron repulsion, spin-orbit coupling, and crystal field splitting.[50] A study of the optical and magnetic data for actinide tetrakis (borohydride) complexes[57] has demonstrated a larger reduction in the spin-orbit coupling constant and Slater parameters, as well as the necessity to include an orbital reduction factor to fit experimental susceptibility curves. These data are consistent with a greater degree of covalent bonding in these complexes than was observed for tris(cyclopentadienyl)lanthanide compounds.

INFRARED SPECTROSCOPY

While infrared spectoscopy has been very useful in the elucidation of structural features of organo-f-element complexes,[58] it is less informative with regard to bonding. Several general comments can be made regarding cyclopentadienyl compounds, however. Correlations have been drawn between the frequencies of certain vibrational modes of coordinated $C_5H_5^-$ and the nature of its bonding. It has been qualitatively concluded from such studies that $(C_5H_5)_3La$ is ionic.[59] This same conclusion has been reached from the observation that inter-ligand coupling is generally very weak in f-element cyclopentadienyl complexes.[60]

More direct evidence for covalent contributions to bonding has been obtained from infrared studies on Lewis bases coordinated to cyclopentadienyl lanthanide complexes, particularly those that are capable of backbonding (CO, CNR, etc.). The changes in ligand stretching frequencies can be correlated with changes in electron density (or orbital population) as a function of coordination to the metal complex. It has been observed that coordination of isocyanides to electropositive metal centers in a σ-only fashion results in an increase of the C-N stretching frequency, whereas if the metal has filled orbitals of the right energy and overlap to donate to unfilled ligand π^* orbitals, the C-N stretching frequency decreases.[61] Isocyanide adducts of lanthanides and actinides generally possess ligand bonds at higher energies than those for the free ligands,[62,63] but trivalent uranium complexes seem to display the smallest increases in the stretching frequencies.[63] This may be interpreted either as an indication of weaker σ-bonding or of π-backbonding. The observation that uranium has a much higher affinity for isocyanide ligands than cerium in direct competition studies[63b] suggests that the π-bonding explanation is correct. This is further supported by the recent observation that tris(cyclopentadienyl)uranium(III) complexes form stable adducts with CO, in which ν_{co} is lowered more than 150 cm^{-1} from that of the free ligand.[24]

NMR SPECTROSCOPY

Solution NMR spectroscopy of organolanthanide and organoactinide complexes is dominated by the paramagnetism of the compounds (except for the diamagnetic nuclei La^{3+}, Ce^{4+}, Yb^{2+}, Lu^{3+}, and Th^{4+}). Unlike many d-transition metal paramagnetic species, however, electron spin state relaxation times are often short enough that line widths are relatively sharp, rendering the lines observable. In general, coupling information cannot be obtained due to line broadening, resulting in the loss of some structural information, but the broad chemical shift ranges result in first-order patterns, simplifying spectral interpretation.

The theory of chemical shifts in paramagnetic species has been discussed extensively in relation to complexes of the f-elements, both in coordination and organometallic environments.[64] From it one can extract information about electronic structure, particularly in cases of high axial symmetry. The isotropic (or paramagnetic) shift, representing the difference between a paramagnetically shifted nucleus and the corresponding chemical shift in a chemically equivalent diamagnetic molecule, is considered to be composed of two terms, the dipolar (or pseudo-contact) term Δ^{dip} and the Fermi contact term Δ^{con} (Eq. (1)).

$$\Delta^{iso} = \Delta^{dip} + \Delta^{con} \tag{1}$$

The dipolar term accounts for shifts due to through-space coupling between the magnetic moment of the observed nucleus and that of the metal-based unpaired electrons. The contact shift term is related to the amount of the free electron spin density at the nucleus. It has been suggested that the contact shift term for a nucleus on a ligand correlates with the extent of covalency in the metal bonding to that ligand,[65] but evaluation of this contribution is complicated by several factors. It is often difficult to resolve the isotropic shift into its dipolar and contact components. This problem has been approached in several ways. In some cases, the dipolar shift term has been assumed to be the sole contribution to the isotropic shift for nuclei removed by more than three or four bonds from the paramagnetic center. This allows evaluation of the dipolar contributions to the shift for closer nuclei, once corrections are made for differing geometric factors.[66] The contact shift term is then simply evaluated as the difference between the dipolar term and the isotropic shift. Other groups have based their calculation of contact terms on electron-spin hyperfine coupling constants calculated with the INDO method.[67] A third approach involves the calculation of dipolar shift contributions from geometric factors and magnetic anisotropy factors derived from optical assignments.[68] The similarity of ring proton contact terms in Cp_3UX systems is taken as evidence of constancy in the ring–metal bonding.

Examination of the ^1H NMR spectra of ring-substituted uranocenes reveals that equivalent ring protons appear at quite different chemical shifts. Since all ring protons should experience the same dipolar shifts (it has been determined that pseudocontact terms can be calculated assuming axial symmetry, even in substituted uranocenes), the differences in the isotropic shifts should be due to differences in the contact terms. Extensive studies have been carried out on ring-substituted uranocenes to determine contact shift contributions for ring protons.[65] They were found to be 10 to 15 ppm larger than those determined for the cyclopentadienyl protons in Cp_3UX compounds. This cannot be simply interpreted as an increase in the covalence of the bonding, however, since there is some question as to the mechanism of transfer of spin density to ligand nuclei. It has recently been suggestd that this occurs through a polarization mechanism, relying on overlap between ligand orbitals and uranium filled 6s and 6p orbitals, making the contact shift insensitive to covalent bonding contributions.[69]

Aside from yielding information about the intrinsic electronic structure of organo-f-element complexes, NMR spectroscopy can be used as a tool to evaluate thermodynamic bond strengths for metal–ligand bonds by the measurement of equilibrium constants for dissociative exchange. A recent study[40] reported a series of Lewis base competition studies for tris(cyclopentadienyl)uranium and -cerium. By addition of a second, free Lewis base (L′) to a solution sample of Cp_3ML and observation of the resulting equilibrium (Eq. (2)), a qualitative order of ligand affinity has been established for uranium.

$$Cp_3U\text{-}L + L' \xrightarrow{K_{eq}} Cp_3UL' + L \qquad (2)$$

Surprisingly, potential π-accepting ligands such as phosphines and phosphites readily displaced hard Lewis bases such as ethers and amines, and it was suggested that the uranium may be acting as a π-base. This π affinity was markedly reduced for the lanthanide complex, consistent with a greater ionic character for cerium.

PHOTOELECTRON SPECTROSCOPY

Gas-phase photoelectron spectroscopy (PES) has emerged as an important tool in studying the orbital energetics of organo-f-element compounds,[70] as one can directly obtain a spectrum of electron binding energies. If one neglects the effects of electron correlation and relaxation in the resulting ion states (Koopmans' theorem), the binding energies can be directly related to molecular orbital energies. The errors introduced by this approximation should be relatively constant within a series of chemically similar molecules, however, which suggests that relative energy differences for such a series will be substantially correct.

The intensity of PES bands also conveys information about the origins of the photoejected electrons. In particular, metal-based electrons have an enhanced cross-section towards He(II) radiation (40.40 eV) with respect to He(I) radiation (21.21 eV). Examination of both the He(I) and He(II) spectra can therefore often aid in the assignment of ionizations due to these electrons. Furthermore, it has been observed that f-electrons have a particularly high cross-section for He(II) radiation, which can help distinguish between d- and f-electron based ionizations.

Photoelectron spectroscopic studies of organo-f-element complexes are almost always accompanied by molecular orbital calculations to provide a model from which to assign the spectrum. Many of these calculations were presented in the section on Theoretical Studies, and the discussions will not be repeated here. It is not entirely proper to discuss PE spectra without the accompanying theoretical treatments, but it can be instructive to compare series of related ionizations in related molecules. By monitoring the position of bands corresponding roughly to ligand ionizations, as compared to metal f (or d) ionizations, a qualitative assessment of covalent character can be obtained.

Bis(cyclooctatetraene) f-element complexes provide a useful series of PE spectra to compare, and some clear trends are observed. Spectra have been reported for uranocene,[71] thorocene,[71] and cerocene.[70b,72] The spectra are qualitatively very similar (see Fig. 9 and Table III), allowing discussion of trends in energy differences. In the spectrum of uranocene, the lowest energy feature is due to ionizations of unperturbed 5f electrons, which explains its absence in the "f^0" Th(IV) and Ce(IV) compounds. This band is usually assigned as the ionization to the virtually atomic $^2F_{5/2}$ state, and the band due to ionization to the $^2F^7{}_{7/2}$ state is predicted to be too weak to be observed.[72] The next two bands are assigned to ionizations from the e_{2u} and e_{2g} ligand-based orbitals. The assignment of the symmetry of these bands is not entirely based upon calculated ordering, however, but also on the observation that the lower energy band increases in relative intensity in the He(II) spectrum, an indicator of f-orbital mixing. For all three metals, the e_{2g} orbital is stabilized more than the e_{2u}, indicating a more stabilizing interaction between ring and metal 6d orbitals than with the 5f orbitals. While no information can be directly inferred from the values of the ionization energies for different complexes, the separation of the e_{2u} and e_{2g} bands (Δ) in each of the complexes is a measure of the magnitude of the difference between d- and f-stabilizing forces for each metal. The cerium complex shows the smallest separation, consistent with its being the most ionic of the three. The PE spectra of substituted uranocenes[73] show no discernible reduction of orbital symmetry, but do show an increase in the ionization potentials of the e_{2u} and e_{2g} orbitals, suggesting that overlap with both 6d and 5f orbitals improves upon alkylation of the ring.

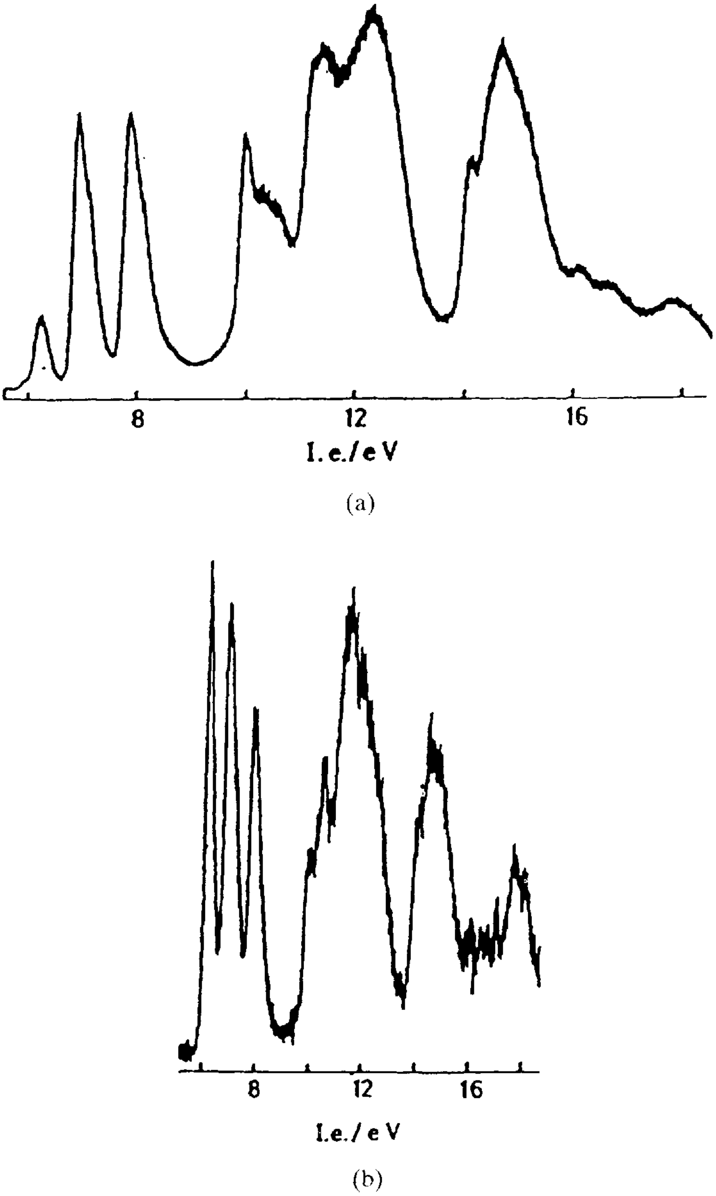


FIGURE 9 (a) He(I) and (b) He(II) PE spectra of uranocene (Ref. 71a).

TABLE III

PES ionization energies and band assignments for $M(COT)_2$ compounds

M	f^n	e_{2u}	e_{2g}	e_{1u}, e_{1g}	$\Delta(e_{2g} - e_{2u})$
Th	-	6.79 eV	7.91 eV	9.90, 10.14, 10.65 eV	1.12 eV
U	6.20 eV	6.90 eV	7.85 eV	9.95, 10.28 10.56 eV	0.95 eV
Ce	-	6.75 eV	7.68 eV	9.98, 10.32 eV	0.93 eV

In the Cp_4M series, the complexes $(C_5H_5)_4M$ and $(C_5H_4Me)_4M$ (M = U, Th) have been studied.[74] As discussed earlier, the valence orbitals of the ligands (derived from the π_2 set) are split under pseudo-T_d symmetry into a t_1 set (interacting only with metal 5f orbitals), a t_2 set, and e set (interacting only with the 6d orbitals). The features of interest in the PE spectra is therefore the t_1-e ordering and separation, as measures of the relative strengths of interactions of the d and f orbitals with the ligands. Although the assignments are not unambiguous,[70a] the assignment of the lowest energy features (except for the unperturbed 5f ionizations) suggests the orbital energy order $t_1 > t_2 > e$, with a t_1-e gap of ca. 1.5 eV. This implies that there is a greater discrepancy in the 6d- and 5f-orbital matches to ligand orbitals than in the COT complexes, consistent with the prediction of relatively little f-orbital participation.[20] It is interesting to note that in Cp_4M complexes, in contrast to the $(COT)_2M$ compounds, those bands that are assigned as possessing 5f character now show a lower intensity increase in the He(II) spectrum than those predicted to have 6d-ligand bonding character. In lower symmetry cyclopentadienyl complexes Cp_2MX_2,[75] the ionizations from the π_2 ligand orbitals are less split by interaction with metal orbitals than either Cp_4M or Cp_3MX,[76] as expected.

Few PES studies have been reported on cyclopentadienyl complexes of the lanthanides. Examination of the spectra for a series of $(C_5H_4Me)_3M$ lanthanide compounds (M = Ce, Pr, Nd, and Sm)[77] has demonstrated that the ionization from orbitals derived from the ring π_2 orbitals form a poorly resolved manifold between 7 and 9 eV; the lack of splitting is interpreted as the lack of interaction of these orbitals with metal orbitals. This suggestion is supported by the observation that there is no change in the intensity profile of the bands in the He(II) spectra. This type of ionic bonding has also been suggested by the PE spectra of the divalent lanthanide complexes $(C_5Me_5)_2M$ (M = Sm, Eu, and Yb).[17]

Although PES studies have clearly demonstrated a greater degree of interaction between metal and ligand orbitals in the actinide cyclopentadienyl complexes than in those of the lanthanide elements, it is instructive to compare the general magnitude of the stabilization to a better understood standard: first row transition metal metallocenes. In general, a stronger covalent interaction between metal d-orbitals and the Cp π_2 orbitals is reflected in an increased ionization potential for the Cp π_2 electrons. The ranges for these ionizations in various classes of cyclopentadienyl complexes is as follows: $(C_5H_5)_2M_T$, 8.4–10 eV; $(C_5H_5)_4An$, 7.4–9.2 eV; $(C_5H_4Me)_3Ln$, 7.0–8.5 eV. It has been inferred from this information[70a] that while the actinide cyclopentadienyl compounds are indeed more "covalent" than their lanthanide counterparts, a substantial amount of ionic character remains in the bonding, when compared to transition element complexes.

CONCLUSIONS

In this Comment, we have presented a sample of the various theoretical and experimental approaches used to determine the extent of covalency in the bonding in organo-f-element complexes. There is a certain speciousness in purporting to classify such molecules as purely ionic or covalent. Most theoretical and experimental evidence points to the general conclusion that organoactinide complexes are more covalent than organolanthanide complexes, and less covalent than analogous transition metal systems. The assignment of the position of a specific system on the "ionic–covalent continuum" is often dependent on the specific probe used. There are particular cases where perturbations to ionic bonding are most evident. For high-valent early lanthanide complexes, such as those of Ce(IV), the high charge-to-radius ratio causes a contraction of the 5d orbitals. This can bring them into appropriate spatial and energetic regimes to interact significantly with organic ligands. Likewise, low-valent early actinides are expected to display the most covalency among these elements; for the later actinides, the 5f and 6d orbitals contract to the extent that covalent bonding is probably not very significant. Consistent with this, the scant organometallic chemistry of the later actinides appears to be quite "lanthanide-like."

The controversy arises in how adequately to account for these perturbations. It is clear that in certain cases both molecular orbital and ionic bonding models possess tremendous utility. Molecular orbital theory can be used to quantitatively predict properties such as magnetic moments and the energies of electronic transitions. A qualitative ionic bonding model incorporating the effects of ion polarizability is attractive, owing to its simplicity relative to rigorous electronic structure methods, and can be very useful to the experimental chemist. Thus, we present no simple answer to the question of covalency in organo-f-element chemistry. We suggest further that no such simple answer exists! Rather, it must be the role of individual researchers to consider the requirements of the physical or chemical properties that they are studying, and to decide for themselves which model will best aid in the interpretation of their experiments.

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