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Photoelectron Spectroscopy of f-Element Organometallic Complexes. 6. Electronic Structure of Tetrakis(cyclopentadienyl)actinide Complexes

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A description of the electronic structure of M(η^5-$C_5H_4CH_3$)$_4$ (M = Th, U) complexes as based upon He I and He II photoelectron spectra and relativistic Xα–SW calculations is presented. Despite the true S_4 symmetry of the molecules, the outermost MO's are grouped as if the complexes have a pure tetrahedral ligation environment. As a consequence, donation to empty metal orbitals appears to be highly dominated by the symmetry requirements. The HOMO in Cp'$_4$U is almost pure 5f in character, and the corresponding $^2F_{5/2}$ final state produced upon ionization is split by operation of a T_d ligand field. The relative intensity variations observed on passing from He I to He II spectra are quite unexpected. It appears that the He II increases of PE signals due to MO's having large metal 6d character are greater than those due to MO's having comparable 5f admixture.

Introduction

The recent growth in the organometallic chemistry of the 5f metals has spurred the need for a better understanding of the interactions between organic ligands and actinide metals. Of particular interest is the magnitude of metal–ligand covalency, a question that has been the subject of considerable experimental and theoretical effort.[2] Gas-phase UV photoelectron spectroscopy (PES) has proven an effective probe of the ground-state electronic structure of such molecules,[3] in large part due to the great variation in ionization cross section of metal- and ligand-based electrons with ionizing photon energy. Thus, these previous studies have exploited the combined use of He I (21.21 eV) and He II (40.8 eV) ionizing sources, and the intensity patterns that result under the two radiations are often significantly different depending on the character of the electron that is being singled out in the photoionization event.[3,4]

In the case of 5f-element complexes, the main point to emerge thus far is that, under He II radiation, 5f atomic orbitals (and MO's formed thereof) show an increase in photoionization cross section relative to those of ligand electrons. The application of these experimental criteria to the PE spectra of highly symmetrical complexes of U(IV) and Th(IV) first provided evidence of significant contributions of both 5f and 6d metal electrons to the metal–ligand bonding. These conclusions have been supported by relativistic Xα–SW molecular orital calculations on these systems.[5] In the case of complexes of lower symmetry, PES has provided unambiguous evidence of significant 5f covalency, and in those cases where analogous transition-metal complexes were available for comparison, the purely experimental PES approach proved capable of probing the aspects of 5f vs. 6d covalency. These results have also been corroborated by relativistic Xα–SW calculations.[5b]

A series of organoactinide complexes that do not have structural analogues in the d-block metals are the highly symmetric, sterically crowded tetrakis(cyclopentadienyl) complexes (η^5-C_5H_5)$_4$M (M = Th, U). Green and co-workers have previously reported a PES study of these complexes[6] and have noted that one ligand-based ionization shows a sizable intensity enhancement upon switching from He I to He II radiation. The spectral assignments advanced were based on the assumption that 5f electrons should exhibit a greater relative intensity increase than should 6d electrons under He II radiation. This assumption has not been thoroughly tested, nor have the proposed assignments been corroborated with electronic structure calculations. We have, therefore, embarked on a detailed experimental and theoretical study of the valence electronic structure of these complexes, and in this paper we report the results of relativistic Xα–SW calculations on Cp_4Th and Cp_4U (Cp = η^5-C_5H_5) in conjunction with the PE spectra of the ring-substituted complexes Cp'$_4$Th and Cp'$_4$U (Cp' = η^5-$C_5H_4CH_3$). The choice of the methylated complexes is based on their superior thermal stability (relative to that of the unsubstituted Cp complexes), which allows higher resolution spectra and, hence, a more precise evaluation of the He I vs. He II intensity patterns.

Experimental Section

The compounds were prepared in a fashion analogous to the literature methods proposed for Cp_4M complexes.[7] They were purified by sublimation in vacuo and gave satisfactory mass spectrometric analyses. The spectra were recorded on a PS-18 Perkin-Elmer spectrometer modified by the inclusion of a hollow cathode discharge source giving a high output of He II photons (Helectros Development Corp.). The spectra were accumulated in the "multiple-scan mode" with the aid of of a MOSTEK computer directly interfaced to the spectrometer. The energy scale of consecutive scans was locked to the reference values of the $^2P_{3/2}$ and He $(1s)^{-1}$ self-ionization lines.

Deconvolutions of the spectra were carried out by fitting the experimental profiles with a series of asymmetrical Gaussian curves after subtraction of background. The areas of bands thus evaluated are estimatd to be accurate to better than 5%. Relevant PES data are compiled in Table I.

Computational Details

Xα–SW calculations on the model complexes Cp_4Th and Cp_4U were undertaken using existing codes that incorporate the quasi-relativistic corrections of Wood and Boring.[8] Atomic coordinates were taken from the crystal structure of Cp_4U;[9] in the case of the structurally uncharacterized Th complex, the same M–C distance was assumed. Both molecules were idealized to D_{2d} symmetry. The initial molecular potential for

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Table I. Photoelectron Spectroscopic Data and Assignments for Cp'_4Th and Cp'_4U

band label	Cp'_4Th			Cp'_4U			assign
	IP, eV	rel intens[a]		IP, eV	rel intens[a]		
		He I	He II		He I	He II	
x				6.25	0.05	0.30	$^2F_{5/2}$; 15e MO
x′				6.52	0.02	0.15	
a	7.25	1.05	1.00	7.32	0.85	0.85	$5a_2$ $14e$ } t_1
b	8.17	1.00 {0.70	1.00 {0.75	8.27	1.00 {0.80	1.00 {0.85	$13e$ } t_2
b′	8.42	0.30	0.25	8.65	0.20	0.15	$9b_2$
c	8.83	0.70	0.85	9.07	0.49	0.70	$9a_1$ $5b_1$ } e

[a] Bands b have been chosen as references because of the lower metal contributions to corresponding MO's.

Table II. Structural Parameters, Sphere Radii, and α Values Used in the Xα–SW Calculations on $(\eta^5\text{-}C_5H_5)_4U$

bond length or angle	value	
	M = Th	M = U
M–C, Å	2.81	2.81
C–C, Å	1.39	1.39
C–H, Å	1.09	1.09
Cp–M–Cp,[a] deg	109.5	109.5

atom	sphere radius, Å		α value	
	M = Th	M = U	M = Th	M = U
outer sphere	4.10	4.10	0.755 28	0.754 17
M	1.66	1.65	0.692 00	0.692 00
C	0.90	0.90	0.759 28	0.759 28
H	0.68	0.68	0.777 25	0.777 25

[a] Cp denotes centroid of C_5H_5 ligand.

Table III. Highest Occupied Orbitals of Cp_4Th and Cp_4U from the Relativistic Xα–SW Molecular Orbital Calculations

orbital energy, eV	symmetry		% metal contributions		
	D_{2d}	T_d	5f	6d	7p
		Cp_4Th			
−4.98[a]	a_2	t_1	14		
−5.00	e		14		
−5.85	b_2	t_2	1	8	2
−5.88	e		1	8	2
−6.50	a_1	e		17	
−6.53	b_1			17	
		Cp_4U			
−3.47[a]	e		86	3	
−5.03	a_2	t_1	23		
−5.05	e		23		
−5.74	b_2	t_2	1	8	2
−5.77	e		1	8	2
−6.26	a_1	e		17	
−6.28	b_1			17	

[a] Highest occupied molecular orbital. The HOMO of Cp_4U is occupied with two electrons.

each was constructed from a superposition of neutral-atom charge densities. The bond lengths, sphere radii, and α values are summarized in Table II. Both calculations were carried out by using a partial wave basis consisting of spherical harmonics through $l = 4$, $l = 3$, $l = 1$, and $l = 0$ on the outer-sphere, metal, C, and H centers, respectively. Our experience has been that a larger basis is unnecessary for such systems.[10] The calculations were converged in a fashion analogous to those for third-row transition-metal systems in which relativistic corrections have been included.[11] Ionization potentials for several of the highest occupied orbitals were explicitly calculated with Slater's transition-state formalism,[12] and because of the high apparent symmetry of the molecules, the remainder of the valence ionization potentials were estimated by using the energetic shift of orbitals that were explicitly calculated. The converged energies and atomic sphere percent contributions of the highest occupied orbitals are listed in Table III and compared in Figure 1.

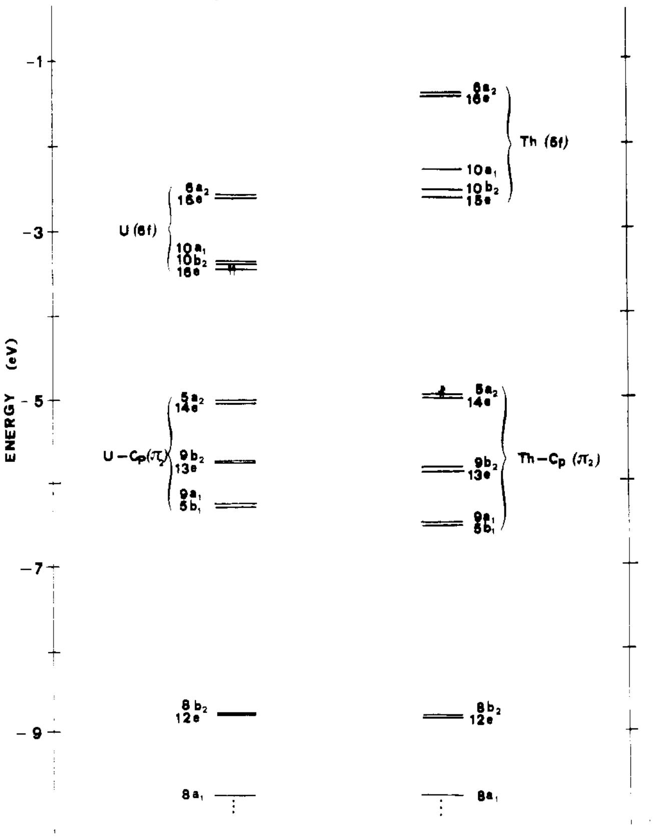

Figure 1. Relativistic Xα–SW eigenavlues for the outermost valence orbitals of Cp_4U and Cp_4Th.

In addition to the relativistic Xα–SW calculations, nonrelativistic extended Hückel (EH) calculations were performed for Cp_4U and the ligand cluster $(Cp)_4$. The EH parameters were taken from a previous EH study of organouranium complexes.[13] Calulations were performed under both the crystallographic S_4 and idealized D_{2d} point symmetries in order to gauge the validity of assuming the higher symmetry. No significant differences in the orbital energetics were found.

Discussion

The complexes Cp_4M have tetrahedral ligation environments, a fact that has been exploited in an earlier investigation[14] of the T_d model complex $U(C_6H_6)_4{}^{4+}$. Previous investigations of met-

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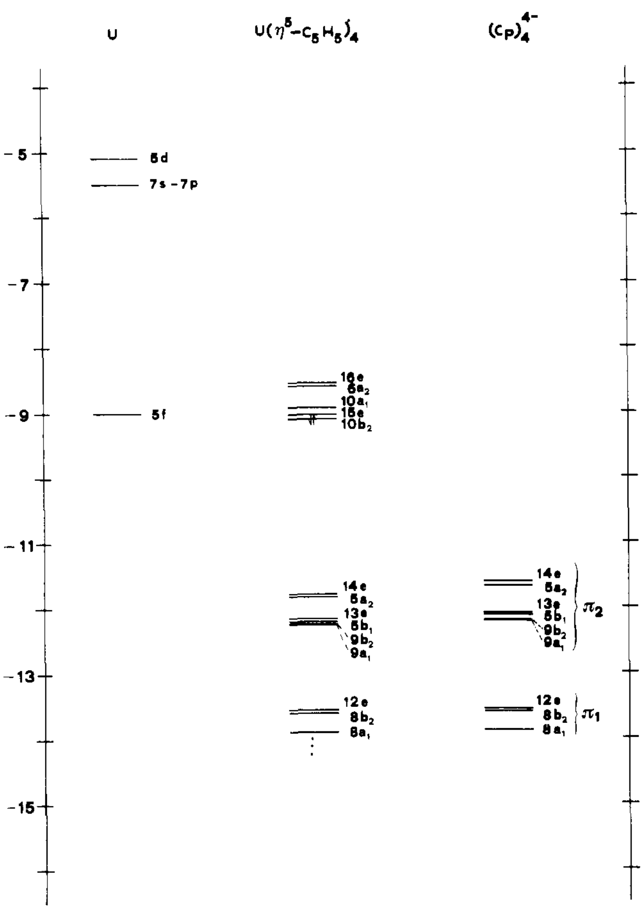

Figure 2. Nonrelativistic extended Hückel eigenvalues for the outermost valence orbitals of Cp_4U and $(Cp)_4$.

Table IV. Nonrelativistic Extended Hückel Eigenvalues and Metal Contributions for Cp_4U

orbital energy, eV	symmetry		% metal contributions		
	D_{2d}	T_d	5f	6d	7p
-9.09	$10b_2$		88	1	
-11.77	14e	t_1	4		
-11.82	$5a_2$		6		
-12.16	13e	t_2		2	2
-12.20	$5b_1$		1	2	2
-12.22	$9a_2$	e		4	
-12.22	$9a_1$			4	

Table V. Comparison of Calculated $X\alpha$–SW Transition-State Ionization Potentials for Cp_4Th and Cp_4U to the Experimental Ionization Potentials of Cp'_4Th and Cp'_4U

orbital	Cp_4Th calcd IP,[a] eV	Cp'_4Th exptl IP,[b] eV
$5a_2$	6.95	7.25 (a)
14e	(7.0)	
$9b_2$	7.79	8.17 (b)
13e	(7.8)	
$9a_1$	8.46	8.83 (c)
$5b_1$	(8.5)	
orbital	**Cp_4U calcd IP,[a] eV**	**Cp'_4U exptl IP,[b] eV**
15e	5.73	6.25 (x), 6.52 (x′)
$5a_2$	7.00	7.32 (a)
14e	(7.0)	
$9b_2$	7.68	8.27 (b)
13e	(7.7)	
$9a_1$	8.22	9.07 (c)
$5b_1$	(8.2)	

[a] Values in parentheses are estimated from the energetic shift of similar orbitals. [b] Band labels are given in parentheses.

al–cyclopentadienyl complexes have indicated that the most important ligand-based valence orbitals in Cp complexes are those that are symmetry combinations of the e_1 (π_2) MO of each Cp ring.[15] A qualitative gauge of the influence of the metal center upon the ligand orbitals is possible by a comparison of the EH results on $(Cp)_4$ and Cp_4U.

The EH energy ordering of the symmetry combinations of the filled π MO's of $(Cp)_4$ under D_{2d} symmetry is shown in Figure 2. Two observations must be made. First, these MO's are energetically grouped in a fashion that is well described by T_d symmetry (hence, thereafter the T_d labeling will be adopted). Second, the most prominent effect of the interligand repulsion is seen in the energy separation between the t_1 and t_2 MO's (0.41 eV) while the e MO remains almost degenerate with the t_2 MO. Previous investigations indicate that in complexes of 5f metals the major effect of the bonded metal upon the ligand framework is due to perturbation of suitable ligand-based MO's by 6p, 5f, 6d, 7s, and 7p subshells,[4,5] which span practically all the irreducible representations of the D_{2d} point group. Nevertheless, the EH calculations seem to indicate (Table IV) that the relevant metal–ligand interactions reproduce those expected in the higher T_d symmetry. Similar results have been obtained by adopting the crystallographic S_4 symmetry for calculations. However, these metal–ligand interactions do not affect the energy dispersion of upper filled MO's on passing from the $(Cp)_4$ cluster to the uranium complex for reasons that are not clear to us. Therefore EH calculations, although of qualitative significance, cannot be conclusive for the interpretation of the spectra.

By contrast, $X\alpha$ calculations in both the SW[4b,c,5,16] and the DVM[17] formalisms have proven capable of providing an adequate description for the assignment of the PE spectra of actinide derivatives. Inspection of the data compiled in Table III indicates that, despite the lower symmetry, the $X\alpha$–SW eigenvalues of the ligand-based orbitals also are energetically grouped essentially as if the molecules were tetrahedral. In the case of Cp_4Th the upper lying MO's are symmetry combinations of the ligand π_2 orbitals, thus resulting in the t_1 ($5a_2 + 14e$), t_2 ($9b_2 + 13e$), and e ($9a_1 + 5b_1$) orbitals. In the case of Cp_4U the HOMO is essentially a pure 5f atomic orbital with small contributions from U 6d and C 2p (π-ring) orbitals while the MO's that follow ($5a_2$–$5b_1$) reproduce those found in Cp_4Th. The admixture of metal contributions into upper lying, ligand-based MO's also fits a tetrahedral scheme; the t_1 orbitals in both Cp_4M complexes are significantly admixed with the M 5f, the t_2 with both M 6d and M 5f, and finally the e with M 6d. The lower lying t_2 ($8b_2$ and 12e) and $8a_1$ MO's follow the same energetic sequence (although with remarkably different energy separations) as found with EH calculations. These represent symmetry combinations of ring π_1 MO's, and apart from the expected small M 7s contribution to the $8a_1$, they have no important contributions from metal subshells.

Valence ionization energies for the molecules studied have been evaluated in the transition-state formalism only for MO's up to $5b_1$ (Table V) because it is well-known that the ionization of lower lying MO's in Cp complexes results in PE bands that are broad and overlapping, precluding any unambiguous assignment.

The He I PE spectra of the Cp'_4M complexes are shown in Figures 3 and 4. They consist of three main bands (labeled a,

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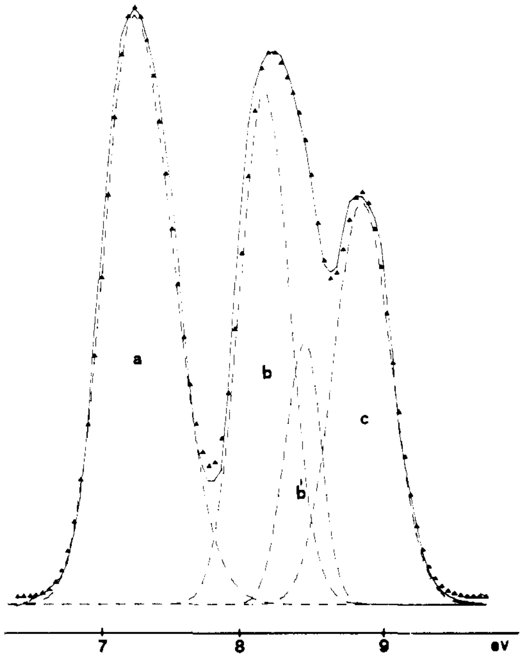

Figure 3. Low ionization potential region of the He I PE spectrum of Cp′$_4$Th.

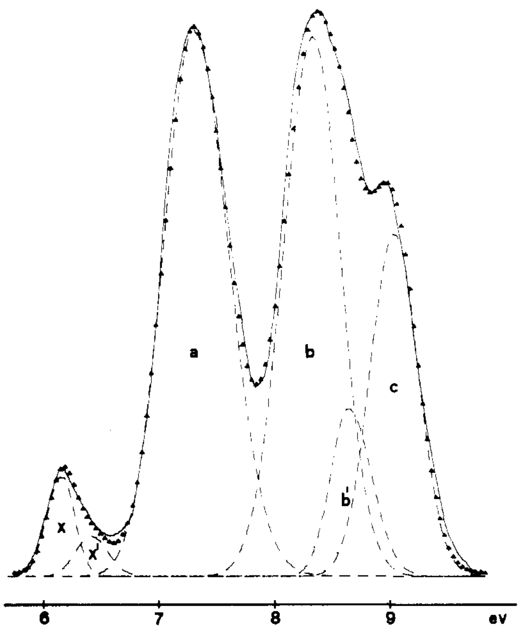

Figure 4. Low ionization potential region of the He I PE spectrum of Cp′$_4$U.

b, and c) in the 7–10-eV region. In addition, a low-intensity, low-energy feature (labeled x) is present in the spectrum of Cp′$_4$U. These general features fit very well into the energy grouping of Xα ground-state eigenvalues. More interestingly, a satisfactory agreement is found between the calculated and experimental ionization potentials (Table V) even though the calculated values are uniformly too low by ca. 0.3 eV. This effect, which is quite often observed in Xα–SW calculations, might be enhanced in the present case due to the omission of the ring methyls in the model compounds used for the calculations. On the basis of these Xα results, bands a–c in the Cp′$_4$Th spectrum must be assigned to production of the final ion states $^2T_1$, $^2T_2$, and ^2E upon ionization from the corresponding MO's. In the case of the uranium complex the onset band x must be assigned to ionization from the metal-based 5f electrons. In actuality for the case of the open-shell Cp′$_4$U, ionizations from t_1, t_2, and e MO's should result in several final ion states because of the coupling of the positive hole (which is formed on ionization) with the open-shell ground state. Nevertheless, the similarity between the spectra of Cp′$_4$U and Cp′$_4$Th suggests that such exchange effects are not significant in the present case.[18]

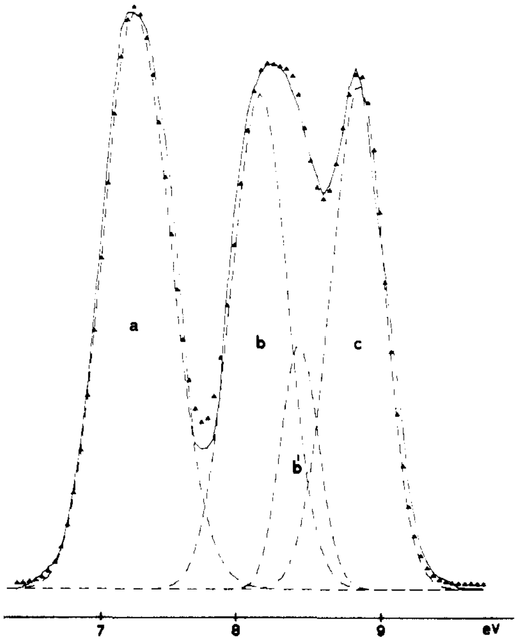

Figure 5. Low ionization potential region of the He II PE spectrum of Cp′$_4$Th.

Deconvolutions of the experimental spectral profiles were performed for bands up to 10 eV (Figures 3 and 4), and relative band areas were corrected for the transmission function of the analyzer (Table I). In both cases relative intensities of bands a:b:c fit the ratio 3:3:2 expected for the occupancies of corresponding MO's. In reality a good fitting of the valley between peaks b and c requires an additional component (b′ in the figures). Nevertheless this extra band can be an artifact due to a not fully appropriate correction of the spectral background. Alternatively, it might be due to an effective splitting of the t_2 MO due to specific metal–ligand interactions or, for instance, to a vibronic Jahn–Teller effect in the $^2T_2$ ion state.

As far as the onset band x in the PE spectrum of Cp′$_4$U is concerned, a good fitting of the experimental profile also requires two components (x and x′ in Figure 4) because the band possesses a defined shoulder on the high ionization energy side. The pattern of final-state structure expected on ionizing one 5f electron from the $^3H_4$ ground configuration of 5f^2 uranium compounds has been discussed previously.[4d–h] It has been shown that, of the $^2F_{5/2}$ and $^2F_{7/2}$ final states that can be reached upon ionization of the ground 5f^2 configuration, only the $^2F_{5/2}$ can result in observable PE bands. The PES intensity ratio of the two final-state peaks, although dependent upon the mechanism of ground-state coupling (Russel–Saunders or j–j), is in both cases extremely unfavorable for detection of the $J = {}^7/_2$ state. Moreover, the energy separation ($^7/_2\xi(5f)$) between the two $J = {}^5/_2$, $^7/_2$ states, obviously not dependent on the coupling scheme, would, in the present case, preclude the observation of the $J = {}^7/_2$ state because the PE $^2F_{5/2}$ peak lies in close proximity to the more intense band envelope a–c, and thus any low-intensity structure due to the $J = {}^7/_2$ state would be hidden.

It is known, however, that, in tetrahedral complexes, the ligand field can act as a weak perturbation capable of splitting the $J = {}^5/_2$ state into E″ and U′ components (in the corresponding double group). Calculation of the energy splitting of the $^2F_{5/2}$ state for several tetrahedral complexes provided an energy separation between the two components ranging from −0.2 to +0.2 eV.[4d] Application of these concepts leads to the conclusion that band x certainly represents the $^2F_{5/2}$ final state most probably split by

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[18] Exchange effects never have been found capable of splitting degenerate ligand-based MO's in PE spectra of U(IV) complexes (see ref 4).

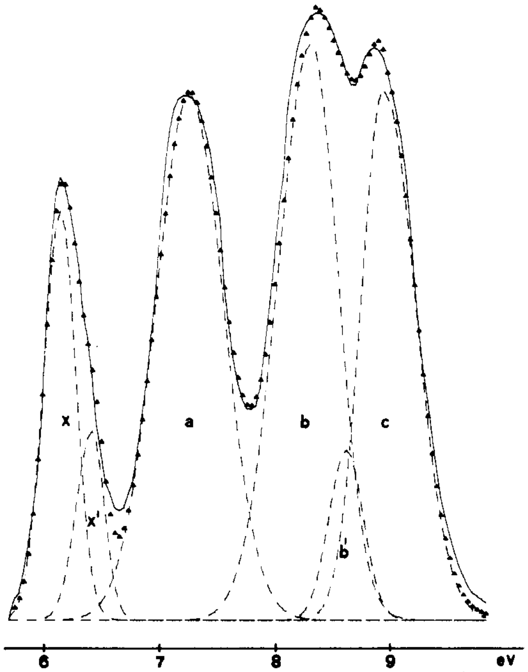

Figure 6. Low ionization potential region of the He II PE spectrum of Cp'_4U.

the nearly tetrahedral ligand field.

When He II radiation is used, notable changes in the relative band intensities are observed (Figures 5 and 6). The most evident effect is the dramatic increase in the intensity of onset band x in the spectrum of Cp'_4U, consistent with the well-known relative increase of PE cross section of metal 5f subshells under He II photons.[3] More interestingly, the relative intensities of the Cp'-based bands a–c also vary considerably in the He II spectra of both complexes; this is consistent with the observations of Green et al. on the Cp_4M complexes.[6] In particular, band c, which we assign to ionization of the e MO, increases in intensity relative to band a, which is due to ionization of the t_1 MO, the effect being more pronounced in Cp'_4U. In Table III it is seen that both the e and t_1 orbitals contain about the same percentage of metal character but that the contribution to the e orbital is from the metal 6d orbitals while that to the t_1 orbital is entirely from the metal 5f orbitals. Thus, within the assumption of the validity of the Gelius model for photoelectron cross sections,[19] the assignment we are presently proposing suggests that with a change from He I to He II radiation the cross section increase for the U and Th 6d subshells is greater than that for 5f subshells. Bands a and b do not change in relative intensity upon switching from He I to He II radiation, which is also consistent with the above notion; it is seen that the metal contribution to the t_2 MO is considerably less than that to the t_1 MO for Cp_4U but that the dominant contribution to the t_2 MO is from metal 6d orbitals.

The spectra presented here for Cp'_4M are very similar to those of Cp_4M reported by Green and co-workers.[6] The first ionization of Cp'_4U occurs ca. 0.1 eV lower than that of Cp_4U, consistent with the expected greater donor ability of Cp' relative to Cp. Similarly, bands a–c for Cp'_4U are all found within ±0.1 eV of the corresponding bands in Cp_4U. Bands a–c of Cp'_4Th are all found ca. 0.3 eV lower in ionization potential than the corresponding bands in Cp_4Th. It therefore appears that methylation of the Cp rings does not affect the ordering of the highest ligand-based ionizations of the complexes.

We are at variance with the assignments presented by Green et al. for Cp_4Th and Cp_4U, however. They first assumed that since the t_2 MO can contain contributions from both the 5f and 6d orbitals of the metal, it was most likely to contain the greatest total metal contribution and hence should show the greatest intensity enhancement under He II radiation. Second, they assume that the cross section increase for 5f orbitals is greater than that for 6d. Thus, their preferred assignment was a:t_1, b:e, and c:t_2 in contrast to our assignment of a:t_1, b:t_2, and c:e. Our calculations do not provide support for their first assumption as we find the t_2 MO to contain the smallest total metal contributions. As mentioned above, the good correspondene between the calculated and observed IP's also casts doubt on their second assumption, for our assignment can only be consistent if the He I/He II cross section increase for the 6d orbitals is greater than that for the 5f orbitals.

Conclusion

The present study provides a detailed description of the electronic structure of Cp'_4M (M = Th, U) complexes based upon both experimental PES data and relativistic Xα–SW calculations. It is seen that, despite the lower S_4 molecular symmetry, the valence MO's are grouped as if the molecules belong to the higher T_d symmetry. The contributions of metal valence AO's to the uppermost MO's also fit a purely tetrahedral scheme. This observation, which seems to indicate a highly symmetric ligand field experienced by the central metal atom, is entirely in accord with the electronic spectral data.[14] From a comparison of the metal contributions to the t_1 and e MO's of both Cp'_4M complexes, it appears that donation into metal 6d orbitals is comparable to or even greater than that into the 5f orbitals. In both complexes the e MO is stabilized by >1 eV more than is the t_1, and in view of the nearly tetrahedral orbital energetics, it is doubtful that ligand–ligand repulsions could account for this difference. The HOMO in Cp_4U is almost pure 5f in character, and upon ionization it results in a $^2F_{5/2}$ final ion state. This final state seems to be split in the E'' and U' components by operations of a tetrahedral ligand field as indicated by the asymmetry of the related PE bands whose Gaussian components (ΔE = 0.27 eV) possess the correct relative areas (Table I) to fit the dimensions of mentioned double-group irreducible representations. As was the case in Cp_2UX_2 complexes, there is a rather small energetic splitting due to the presence of the bonded ligands.

Finally, we must note that from a purely experimental point of view, the main argument to emerge from the present study is that any evaluation of the metal–ligand 5f vs. 6d covalency as based on a comparison of He I and He II PE intensity patterns must be handled with care. One is on safe ground only by using a purely experimental approach applied to a series of isostructural species including both 5f and *n*d (*n* = 4, 5) metal complexes.[4e,g] In other cases, especially when a highly symmetric ligand field can result in specific, symmetry-driven metal–ligand interactions, the guidance of a suitable theoretical approach is highly demanded.[4b,c,5a]

In this context two observations must be made: (i) there is no doubt that under He II photons the increase of the 5f PE cross section is higher than that of C_{2p}, and (ii) the He II PE cross section of 6d subshells relative to C_{2p} can be only extrapolated from the trend observed for *n*d electrons (4d > 3d ≃ 5d > C_{2p}).[20] Extension of these concepts leads to the conclusion that PE signals due to ionizations from MO's having large metal 6d character can also be more intense than those due to C_{2p} MO's,[20] and further, if we trust the present theoretical results, it would appear that the He II PE cross-section increase for Th and U 6d orbitals is greater than that for the 5f orbitals. It is clear, however, that further experimental and theoretical investigations are desirable to provide deeper insight into this aspect.

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