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Photoelectron Spectroscopy of f-Element Coordination Compounds. 1. β-Diketonate Complexes of Uranium(IV), Thorium(IV), Zirconium(IV), and Dioxouranium(VI)

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Photoelectron spectra of some β-diketonate uranyl complexes are reported. They provide information about the ordering of the upper four molecular subshells (belonging to π_g, π_u, σ_u, and σ_g symmetry species) localized on the uranyl ion which yields, in turn, insight into the nature of the bonding in the uranyl ion. It appears that metal 5f covalency is of major importance in this species. The spectra also give information about the bonding between the uranyl moiety and the equatorial ligands: the uranyl ϕ_u orbital is shown to be intimately involved in such bonding. Photoelectron spectra of some tetrakis(β-diketonate)actinide complexes indicate that metal–ligand bonding is dominated by σ-type overlaps. The differences between the photoelectron spectra of transition-metal (Zr) and actinide (Th, U) complexes suggest substantial involvement of the metal 5f subshell in the bonding molecular orbitals of the actinide complexes. The spectra of the uranium(IV) complexes each contain peaks associated with ionization of the metal 5f subshell.

Introduction

Photoelectron spectroscopy (PES) has been shown to be a powerful technique for the elucidation of details of the electronic structure and bonding in classical coordination and organometallic compounds of transition elements.[2] Although the electronic structures of actinide complexes are far from being well understood, very few PES measurements have been reported for such species. We were prompted, therefore, to embark on an extensive study in this area. Some of our results on organometallic actinide complexes have been reported already.[3]

In the present paper we report photoelectron (PE) spectra of some β-diketonates of uranium(IV), thorium(IV), and dioxouranium(VI). Spectra of tetrakis(acetylacetonate)zirconium(IV) are also included for purposes of comparison.

Experimental Section

Materials. The β-diketone ligands pentane-2,4-dione (acacH), 1,1,1-trifluoropentane-2,4-dione (tfaH), and 1,1,1,5,5,5-hexafluoropentane-2,4-dione (hfaH) were obtained from commercial sources and were twice distilled before use in synthetic procedures.

$U(acac)_4$, $U(tfa)_4$, $Th(acac)_4$, and $Zr(acac)_4$ were synthesized by literature[4] methods and were purified by recrystallization and vacuum sublimation. Previous mass spectroscopic measurements indicate unambiguously that these complexes exist as monomeric species in the vapor phase.[5] Anhydrous $UO_2(acac)_2$ and $UO_2(hfa)_2$ were obtained by heating the monohydrated parent derivatives in vacuo[6] and were purified by vacuum sublimation. Their mass spectra contained very intense peaks at m/e 463 and m/e 684, respectively, indicating the exclusive presence of monomeric species in the vapor phase.

The monohydrated complex $UO_2(acac)_2{\cdot}H_2O$ was itself prepared by standard methods.[4] $UO_2(hfa)_2{\cdot}H_2O$, apparently not reported previously, was prepared by refluxing hfaH with UO_2Cl_2 in CCl_4 for 12 h. A yellow crystalline solid was obtained after concentrating and cooling of the resultant solution. Elemental analysis and IR spectra indicated the yellow solid to be $UO_2(hfa)_2{\cdot}H_2O$.

Measurements. The photoelectron spectra were obtained on a commercial Perkin-Elmer PS 18 photoelectron spectrometer using the heated probe inlet system. The spectra were recorded at the following temperatures: $UO_2(acac)_2$, 194 °C; $UO_2(hfa)_2$, 120 °C; $U(acac)_4$, 135 °C; $U(tfa)_4$, 99 °C; $Th(acac)_4$, 138 °C; $Zr(acac)_4$, 145 °C. All the spectra were reproducible over a large range of temperatures around those reported above. Spectra were calibrated by reference to signals due to admixed xenon and argon. Band areas used in the intensity arguments were corrected to allow for the variation of the analyzer transmission function with electron kinetic energy.

Results

The He I PE spectra of $UO_2(acac)_2$ and $UO_2(hfa)_2$ each contain five distinct bands in the low ionization energy (IE) region (labeled A, B, X, Y, C in Figure 1), the last of which has a pronounced shoulder on its low IE side. The bands in the PE spectrum of $UO_2(hfa)_2$ show a general shift to higher IE as compared with those for $UO_2(acac)_2$, and, in addition, the second band displays a pronounced shoulder (B in Figure 1) not apparent in the spectrum of $UO_2(acac)_2$. The higher energy region of both uranyl spectra contains only diffuse overlapping bands similar to those in the spectra of the isolated acacH and hfaH molecules.[7] They relate to ionizations from orbitals forming the σ framework of the ligands; these are unlikely to be involved in the metal–ligand bonding. This region of the spectra will not be considered further. Ionization energies and relative intensities for the low-energy bands of the uranyl spectra are collected in Table I.

The He I PE spectra of the tetrakis(β-diketonate) complexes (Figures 2 and 3) are considerably more complicated than those of the uranyl complexes but each contains five bands (labeled A, B, B′, B″, C) in the low-energy region. In the spectrum of $Th(acac)_4$ bands B and B′ are better resolved than in the spectrum of $Zr(acac)_4$ while a new band, B_x, appears as a shoulder on the low-energy side of band B′. In the spectrum of $U(acac)_4$ this band is somewhat better resolved, but the most striking feature is a weak band at the onset of the spectrum having no counterpart in the spectra of the other tetrakis compounds.

The PE spectrum of $U(tfa)_4$ is clearly analogous to that of the parent compound $U(acac)_4$. The shift of all the bands to higher IE's observed in the PE spectra of fluorinated ligand containing complexes is clearly attributable to the high electronegativity of the fluorine atoms.[7] Ionization energies and intensity data for the tetrakis complexes are reported in Table II.

Discussion

PE spectra of compounds studied in the present work are best interpreted in terms of a molecular orbital (MO) model using a basis set of localized orbitals. Similar qualitative methods have proved useful as an aid to assignment of PE spectra of large molecules.[8] Conventional quantitative MO methods are effectively precluded by the presence of a heavy-metal atom in each of the molecules studied.

Molecular IE's will be related to orbital energies via Koopmans theorem;[9] since differential rescaling effects are unlikely to lead to a reordering of levels in the ionic states obtained upon ionizing electrons from the ligand manifold and in all the complexes reported in the present work, with the exception of the uranium ones, the upper filled MO's are expected to be mainly ligand in character. Turning attention first to an isolated β-diketonate anion, the effective ligand in the studied complexes, consideration based on simple Hückel theory suggests that the three uppermost electronic subshells are respectively the in- and out-of-phase combination of oxygen lone pairs located in the molecular plane and the topmost

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Table I. Ionization Energies (eV) and Relative Band Intensities (in Brackets) of $UO_2(acac)_2$ and $UO_2(hfa)_2$[a]

band system	$Be(acac)_2$	$Be(hfa)_2$	$UO_2(acac)_2$	$UO_2(hfa)_2$	assignment
A	8.41 [1.00]	10.39	8.40 [1.00]	10.05 [1.00]	$b_{1u} + b_{3g}$ (π_3)
B	9.67 [1.38]	11.66	9.65 [2.36]	11.10 11.40 [1.82]	$b_{1g} + b_{3u}$ (n_-) $b_{2g} + b_{3g}$ (π_g)
X			10.30 [0.37]	11.85	b_{1u} (σ_u)
Y			10.80 [0.60]	12.30	$b_{2u} + b_{3u}$ (π_u)
C			11.40 [1.56]	13.05 [1.50]	a_g (n_+)
C′	11.13 [1.10]	12.96	11.80	13.45	b_{2u} (n_+) + a_g (σ_g)

[a] The data for beryllium β-diketonate complexes are reported for comparison (taken from ref 7).

Table II. Ionization Energy Data (eV) and Relative Band Intensities (in Brackets) of the Tetrakis(β-diketonate) Complexes

band system	$Zr(acac)_4$	$Th(acac)_4$	$U(acac)_4$	$U(tfa)_4$	assignment
			6.65	7.83	metal 5f
A	7.95 [2.0]	7.85 [2.0]	7.75 [2.0]	9.03	$b_1 + b_3$ (π_3)
B	8.95 [4.2]	8.75 [3.1]	8.70 [3.2]	9.95	$a + b_2$ (π_3), $a + b_1$ (n_-)
B_x		9.40	9.25	10.20	
B′	9.75 [2.1]	9.60 [1.9]	9.45 [1.9]	10.45	$b_2 + b_3$ (n_-)
B″	10.10	10.05	10.05	11.00	
C	11.35	11.40	11.40	12.45	$a + b_1 + b_2 + b_3$ (n_+)

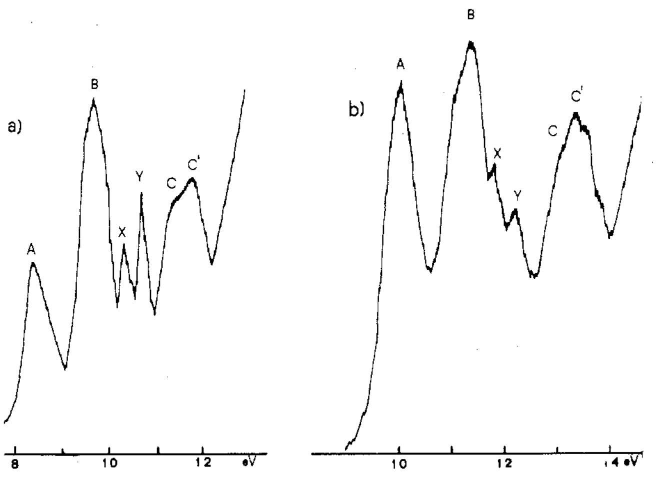

Figure 1. Photoelectron spectra of $UO_2(acac)_2$ (a) and $UO_2(hfa)_2$ (b), low-energy region.

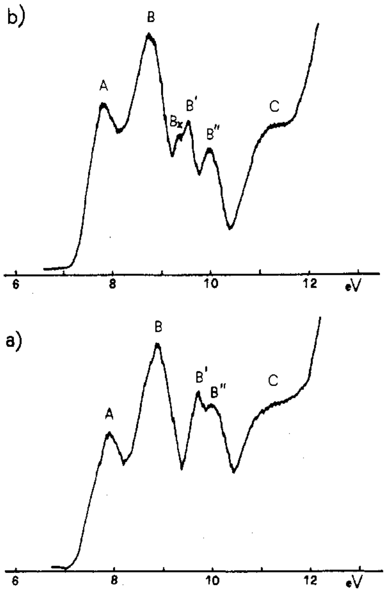

Figure 2. Photoelectron spectra of $Zr(acac)_4$ (a) and $Th(acac)_4$ (b), low-energy region.

out-of-plane π orbital.[7] These MO's are conventionally labeled respectively u_+, u_-, and π_3, according to Evans et al.[7] The IE's of these MO's in metal complexes can be estimated roughly by reference to the PE spectra of other metal β-diketonate complexes[7] and, in particular to that of $Be(acac)_2$ (Table I) whose He I[7] and He II[10] PE spectra (Table I) are consistent with a model in which interligand and metal–ligand interactions are of only minor importance as compared with the shift in ionization energies induced by the electrostatic potential due to the metal ion.

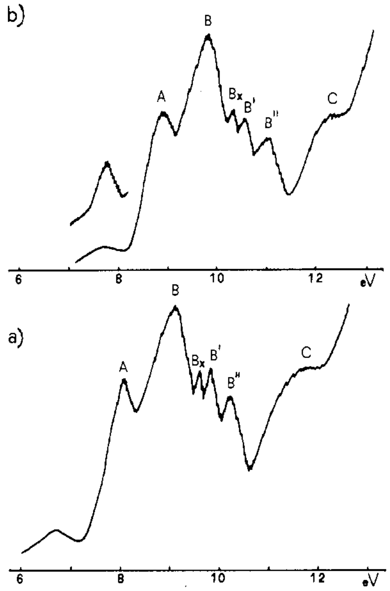

Figure 3. Photoelectron spectra of $U(acac)_4$ (a) and $U(tfa)_4$ (b), low-energy region.

Uranyl β-Diketonate Complexes. In the bis(β-diketonate)uranyl complexes the in-phase and out-of-phase combination of n_-, n_+, and π_3 MO's generate new symmetry orbitals whose transformation properties depend on the point group of the complex. Structural data for monomeric $UO_2(acac)_2$ in the vapor phase has not as yet been reported. However, consideration of the structure reported for the monoclinic $UO_2(acac)_2{\cdot}H_2O$ complex[11] suggests a rectangular-bipyramidal structure as the most probable for the anhydrous complexes. This structure belongs to the D_{2h} point group. In this point group the symmetrized combinations of the ligand orbitals transform as indicated in Figure 4. The accidental degeneracy of each pair of new orbitals will not be removed unless one or both of them is not involved in some interligand and/or metal–ligand interaction. It seems probable

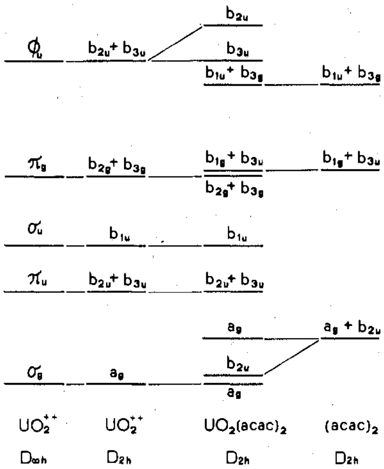

Figure 4. Qualitative molecular orbital scheme for $UO_2(acac)_2$ (D_{2h}).

that significant interligand nonbonded interactions can be ruled out because of the very large interligand distance. The bonding metal–ligand interactions are best considered in terms of uranyl group–equatorial ligand interactions. In fact the optical adsorption spectra of a wide range of uranyl complexes[12] indicate that the ground and excited electronic states are essentially characteristic of the UO_2^{2+} unit.

Accurate overlap calculations[13] indicate the following ground-state configuration: $(\pi_g)^4(\sigma_g)^2(\pi_u)^4(\sigma_u)^2$. The ordering of the low-lying empty uranyl orbitals (ϕ_u and δ_u in $D_{\infty h}$) is not easy to determine. In the axial field approximation ϕ_u should be lower than δ_u. On the other hand, the ϕ_u subshell can be destabilized through an interaction with the equatorial ligand. Some insight into this problem is provided by spectral data for the trans uranium oxycations NpO_2^{2+}, NpO_2^+, and PuO_2^{2+}. Eisenstein and Pryce[14] assigned the ground-state electronic configuration of the NpO_2^{2+} ion to a ϕ_u^1 state while a δ_u^1 state was found to be only 200 cm^{-1} higher in energy. For the PuO_2^{2+} and NpO_2^+ cations a $(\delta_u)^1(\phi_u)^1$ ground-state configuration was proposed.[15] Moreover recent careful studies of the low-temperature single-crystal optical adsorption spectrum of $Cs_2UO_2Cl_4$ in different polarizations indicate a lowest excited configuration $\sigma_u^1\delta_u^1$ rather than $\pi_u^3\delta_u^1$. These considerations suggest that the ground configuration of the uranyl ion should be written as $(\pi_g)^4(\sigma_g)^2(\pi_u)^4(\sigma_u)^2...\delta_u\ \phi_u\ {}^1\Sigma_g^+$ ($D_{\infty h}$).

In the β-diketonate uranyl complexes, any twofold degeneracy can, in principle, be removed by the low molecular symmetry (D_{2h}). However, the low-symmetry perturbation is expected to be of minor importance,[12] and it is expedient for our present purposes to retain a labeling system based on the $D_{\infty h}$ point group. The energies of the occupied uranyl orbitals relative to those for the equatorial ligand subshells cannot be deduced a priori. The ordering pictured in Figure 4 has been set up on the basis of the assignment of the PE spectra of the uranyl complexes discussed below.

In $UO_2(acac)_2$ the large distance (2.4 Å)[11] between the uranyl group and the equatorial ligands precludes significant interactions. Therefore the ligand π_3 systems ($b_{1u}+b_{3g}$) should be essentially nonbonding and give rise to a single PE band. Band A in the PE spectra of both $UO_2(acac)_2$ and $UO_2(hfa)_2$ probably represents ionization from these orbitals (Figure 4). Notice, in passing, that the IE's of the bands in question closely coincide with the π_3 IE's in PE spectra of $Be(acac)_2$ and $Be(hfa)_2$ (Table I).

The n_- equatorial ligand orbitals ($b_{3u}+b_{1g}$) are also expected to behave as nonbonding orbitals in the β-diketonate uranyl complexes. Their localization properties do not allow, on overlap grounds, strong interaction with any orbitals localized on the uranyl group. Ionizations from these orbitals probably give rise to the second band B in the $UO_2(acac)_2$ PE spectrum. Again comparison with the case of $Be(acac)_2$ lends support to this assignment. However, the latter assignment poses some problems. In particular the intensity of band B is twice that of band A: this observation finds no counterpart in the PE spectra of other β-diketonate complexes studied to date,[7] where, in general, π_3 and n_- bands have similar intensity. Possibly ionizations from subshells other than $b_{1g}+b_{3u}$ (n_-) are associated with band B. Indeed the corresponding band in the spectrum of $UO_2(hfa)_2$ shows a distinct low-energy shoulder. It is unlikely that the ligand orbitals $b_{2u}+a_g$ (n_+) will give PE signals overlapping with the n_- bands; n_- and n_+ ionizations are generally well separated. For example $E_{n+}-E_{n-}=2.6$ eV in the PE spectrum of $Be(acac)_2$ while in Li(hfa) (where the metal–ligand bonding is likely to be mainly ionic in character) the $E_{n+}-E_{n-}$ separation is 2.04 eV (Table III). A more tenable assignment for the extra band is to an ionization associated with orbitals localized on the uranyl framework. Furthermore the low-intensity bands X and Y that follow band B in the spectra of $UO_2(acac)_2$ and $UO_2(hfa)_2$ are also likely to relate to orbitals of dominant uranyl character. Their low intensities suggest moreover some participation of the uranium 5f orbitals, whose He I cross sections have been found to be generally lower than the carbon[3] or oxygen[18] 2p cross sections. Therefore we are faced with the assignment of at least three ionizations from orbitals based mainly on the uranyl moiety. The MO ordering in the uranyl group discussed previously would suggest the assignment of the three bands respectively to the σ_u, π_u, and σ_g uranyl orbitals. However, such an assignment is questionable because the intensities of the corresponding PE bands are not as expected on the basis of both the occupancy and composition of the corresponding orbitals. In fact, even if the intensity of the "extra-band" in the spectra of $UO_2(acac)_2$ and $UO_2(hfa)_2$ cannot be deduced directly, it can be roughly evaluated by making a reasonable allowance for the $b_{1g}+b_{3u}$ (n_-) contribution to the bands B.[19] It then becomes apparent that the intensity exceeds that of the bands X or Y and is in fact comparable with that of band A (Table I). Due to the uranium 5f contribution (vide supra) the π_u and σ_u cross sections are expected to be smaller than those of the $b_{3g}+b_{1u}$ (π_3) and $b_{1g}+b_{3u}$ (n_-) ligand orbitals, whereas for the π_g and σ_g uranyl orbitals, having some uranium 6d contributions, cross sections comparable to those of the ligand orbitals can be expected.[20] These considerations lead us to assign the low-intensity bands X and Y to uranyl orbitals of ungerade symmetry. Their relative intensities, 1:1.6, strongly support the assignment respectively to the σ_u and π_u orbitals. The stronger "extra-ionization" probably relates to the uranyl orbital of g type.

Table III. Ionization Energy Differences between the Low-Energy Bands in Some β-Diketonate Complexes

	E_{A-B}, eV	E_{B-C}, eV	E_{A-C}, eV
$UO_2(acac)_2$	1.25	1.95	3.2
$UO_2(hfa)_2$	1.33	1.9	3.24
$Be(acac)_2$	1.26	1.36	2.72
$Be(hfa)_2$	1.27	1.3	2.6
Li(hfa)	0.9	1.1	2.04

The choice between the π_g and σ_g orbitals is rather difficult. However, given that the intensity of the band in question is roughly comparable to that of band A (attributed to the ionizations of the accidentally degenerate $b_{1u}+b_{3g}$ (π_3) orbitals), we feel confident to assign this ionization to the π_g uranyl orbital. Thus, the following order for the upper filled uranyl levels in the β-diketonate complexes merits attention (Figure 4): $\pi_g>\sigma_u>\pi_u>\sigma_g$. There is no clear indication in the spectra of $UO_2(acac)_2$ and $UO_2(hfa)_2$ of the σ_g ionization; it probably lies in the region of the rather intense structure following the band Y. The relationship between this structure (C, C′) and that observed in the same spectral region for $Be(acac)_2$ or $Be(hfa)_2$ is quite clear. In this region one expects ionizations from the equatorial ligand orbitals of symmetry $b_{2u} + a_g$ (n_+) (Table I).

Measurements of intensity of the band C–C′ relative to that of the first band A indicates a 3:2 ratio rather than the ratio 1:1 observed in the beryllium parent compound (Table I). The σ_g ionization could well be responsible for the extra intensity. Moreover the origin of the defined shoulder appearing in the spectra of both $UO_2(acac)_2$ and $UO_2(hfa)_2$ could be connected with such an ionization. However, even if this assignment cannot be fully ruled out, a comparison between the IE's related to the equatorial ligand orbitals in the uranyl β-diketonate complexes and in some parent derivatives of other metals (Table III) suggests an alternative assignment. It appears that the band C in the spectra of uranyl complexes is at higher IE than, for example, in beryllium analogues. Interaction between the b_{2u} (n_+) ligand orbital and the b_{2u} component of the π_u uranyl orbital (D_{2h} symmetry) is unlikely to account for this stabilization: the π_u PE band is unsplit in the spectra of both uranyl complexes. A more attractive explanation for the stabilizing effect can be found in terms of a strong interaction involving the b_{2u} component (D_{2h} symmetry) of the virtual ϕ_u level (Figure 4). This interaction is favored on group overlap grounds and could well remove the accidental degeneracy of the b_{2u} and a_g (n_+) ligand orbitals. As a consequence we feel more confident to assign the C shoulder to the a_g (n_+) ionization and the main component C′ to the nearly degenerate σ_g (uranyl) and b_{2u} (n_+) orbitals (Figure 4).

Tetrakis(β-diketonate) Complexes. X-ray diffraction measurements on $Zr(acac)_4$, $U(acac)_4$, and $Th(acac)_4$ crystals indicate a nearly square-antiprismatic arrangement of oxygen atoms around the metal and an effective D_2 symmetry.[21] The same symmetry has been assumed for the vapor-phase species. Due to this low symmetry the assignment of the PE spectra of these complexes, even qualitatively, poses difficulties. In the D_2 point group the symmetry-adapted linear combinations (SALC's) of the ligand orbitals span all the irreducible representation of the molecular point group: $4\pi_3 \rightarrow a + b_1 + b_2 + b_3$, $4n_- \rightarrow a + b_1 + b_2 + b_3$, $4n_+ \rightarrow a + b_1 + b_2 + b_3$. The same is true for the sets of valence orbitals of the metal atoms present in the complexes. The consequent possible mixing of ligand and metal symmetry orbitals would superficially appear to prevent development of a qualitative picture of the bonding in the tetrakis complexes based on factoring an approximate one-electron matrix. Therefore the spectra will be interpreted mainly through arguments based on comparison with other related spectra.

We consider first the diffuse bands C, a feature common to the spectra of $Zr(acac)_4$, $Th(acac)_4$, and $U(acac)_4$. This band shows little variation in IE in the series of compounds studied (Table II); the IE's are in all cases close to that for the n_+ bands in the spectrum of $UO_2(acac)_2$. Therefore we assign the bands C to the unresolved n_+ ligand SALC's. Although the large number of bands present in the lower energy region of the spectra precludes simple interpretation, the trend in the spectral pattern on traversing the series from the Zr(IV) to the U(IV) complex seems to indicate that the spread of the energy levels does not always depend on specific metal–ligand interactions. The first two bands (A, B), falling in the region where the π_3 ionizations are expected, show a separation that depends little on the metal atom present in the complex (Table II). The effective square-antiprismatic geometry of the tetrakis complexes means that the central metal atom is sandwiched between two pairs of ligands containing an approximately square arrangement of oxygen atoms. The square formed by the four upper oxygen atoms is twisted through an angle of 45° with respect to the lower square and, consequently, each of the upper oxygen P_z orbitals lies between pairs of corresponding orbitals of the bottom ligands. This particular structure with a fairly small distance between the two ligand planes[22] allows interligand interactions to remove the degeneracy of the four π_3 SALC's. Nodal considerations suggest that the a and b_2 orbitals, i.e., "symmetric" combinations between the π_3 ligand orbitals, may be stabilized with respect to the antisymmetric combinations b_1 and b_3 (Figure 5).

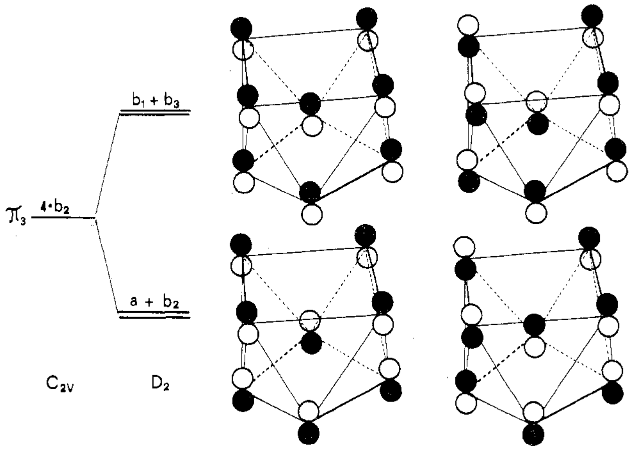

Figure 5. Pictorial representation of the SO's (D_2 symmetry) from the π_3 ligand orbitals. The tich-set edges refer to the edges spanned by the ligand rings.

Bands A and B could well be connected with ionizations from these two species of molecular subshell even though their intensity ratio (Table II) suggests that the intense band B represents some additional ionization process. The observation that the A–B IE separation is slightly higher in $Zr(acac)_4$ than in the actinide complexes is consistent with such an assignment, since the shorter distance between the two planes defined by each pair of ligands in the former complex[22] results in a stronger interligand interaction.

Having now assigned the ionizations related to the π_3 and n_+ SALC's, it becomes clear that the rest of the bands present in the 9.0–10.5-eV region must be assigned to the n_- SALC's. Considering the different spectral patterns on going from $Zr(acac)_4$ to the actinide complexes it can be argued that the metal atom plays a major role in determining the splitting of the above n_- SALC's. Group overlap considerations suggest that in $Zr(acac)_4$ the most favorable interaction involves the $4d_{xz}$ and $4d_{yz}$ metal orbitals (b_2 and b_3 in D_2 point group). Thus, we tentatively assign the two ill-resolved bands having maxima at 9.75 and 10.10 eV, respectively, to the ionizations from the b_2 and b_3 SALC's derived from the ligand n_- orbitals. The remaining two a and b_1 subshells can be associated with the intense band B. The intensity ratios between the low-energy bands are in accordance with our overall assignments. In the spectra of the actinide complexes the presence of an extra band (B_x) that finds no counterpart in the spectrum of $Zr(acac)_4$ together with a more defined splitting of the B′ and B″ bands seems to indicate stronger metal–ligand interactions. The possibility that exchange effects in the ionic states, due to coupling of hole states with unpaired electrons of the uranium atom, account for the extra band B_x can be dismissed on the grounds that the same extra band is present in the spectrum of the thorium complex where there are no unpaired electrons.

It is again difficult to identify which metal orbitals most strongly involve the metal–ligand interaction; however, overlap consideration seems to indicate the $f_{x(5z^2-r^2)}$, $f_{z(x^2-y^2)}$, and $f_{y(5z^2-x^2)}$ uranium orbitals (belonging respectively to the b_3, b_1, and b_2

symmetry species). On the basis of this simple consideration we tentatively assign the bands B_x, B', and B'' in the PE spectra of actinide complexes to the b_3, b_2, and b_1 orbitals essentially n_- in character although it is difficult to be certain as to their relative ordering.

The spectrum of $U(tfa)_4$, not discussed up to now, is clearly analogous to that of $U(acac)_4$.

Considering only the 5f orbitals, when dealing with the metal–ligand interaction in the actinide complexes, we, tacitly, excluded any contribution from the 6d actinide orbitals. However, there has been some speculation that 6d covalency is important in the bonding in the actinide organometallic[23] or coordination compounds.[24] Therefore, even if interaction involving both the 5f and 6d orbitals cannot completely be excluded, the observation that the spectral pattern for the actinide complexes is different from that for $Zr(acac)_4$ is consistent with the idea that different types of metal orbitals are involved in the bonding in the actinide complexes.

Finally we turn to the low intensity band present at the onset of the spectra of the two uranium complexes. Its low intensity and its absence in PE spectra of both $Th(acac)_4$ and $Zr(acac)_4$ suggest the assignment to the $^2F_{5/2}$ final state component derived from the uranium $5f^2$ ground-state configuration. On ionizing one electron from the U(IV) $^3H_4$ ground term, two multiplet levels, $^2F_{5/2}$ and $^2F_{7/2}$, are expected. On a pure atomic model their separation is $3\cdot{}^1/_2\xi$, where ξ is the one-electron spin–orbit coupling constant ($\xi \simeq 0.2$ eV).[25] The ligand field can further split each of these levels but it has been shown that, generally, the field acts as a very weak perturbation.[26] The relative probabilities of reaching the two final states are

$$\frac{P_{J=5/2}}{P_{J=7/2}} = \frac{1.714}{0.286}$$

in the L–S coupling scheme.[27] The probability of reaching the $J = 7/2$ state is further reduced in an intermediate coupling scheme and completely vanishes in the J–J limit.[26] It follows that the intensities of the $2F_{7/2}$ final state in the PE spectra of $U(acac)_4$ and $U(tfa)_4$ are expected to be extremely small. They are probably obscured by the onset of the very intense PE bands associated with ligand ionizations.

Conclusion

The study of the PE spectra of some β-diketonate uranyl complexes provides some novel information concerning (i) the energies of the four upper filled orbitals localized on the O–U–O unit and (ii) their ordering with respect to the orbitals localized mainly on the equatorial ligands. The PE data suggest that the π_g uranyl ionization precedes that associated with the σ_u subshell. This conclusion contrasts with those drawn both from optical adsorption spectroscopy and from a consideration of sophisticated overlap calculations. It should be said, however, that simple overlap arguments are not adequate, in themselves, to set up the electronic structure of the uranyl group. In fact both the π_u and σ_u uranyl orbitals can be more stabilized with respect to the π_g one due to the lower O_{2p}–U_{5f} energy separation compensating for the poorer corresponding overlap interaction. Furthermore the trend in the energies of the optical electronic transitions do not necessarily reproduce the sequence of the ground state occupied and virtual molecular orbitals, these energies being also dependent on the electron repulsion terms. As far as the bonding in these uranyl complexes is concerned, PE data suggest a strong involvement of the uranium 5f orbitals in the "apical" primary bonds. The equatorial bonding seems to be due to the ligand oxygen lone-pair symmetric combination (n_+) and the uranyl ϕ_u orbital. This kind of bonding is in tune with the increased U–O (apical) distance observed in the complex $UO_2(acac)_2$ as compared with the corresponding one in more "ionic" uranyl complexes. In fact our bonding scheme introduces electron density into the ϕ_u orbital, thus lowering the apical bond strength because of the increased electrostatic repulsion. In the actinide tetrakis complexes the metal–ligand bonding appears to be mainly σ in character and involves overlap between the antisymmetric ligand oxygen lone-pair combination (n_-) and the 5f actinide orbitals. Even if some 6d contribution to the bonding cannot be ruled out on a purely experimental basis, the different spectral patterns observed on going from $Zr(acac)_4$ to the actinide complexes suggest that the role of the 5f orbitals in bonding is of dominant importance.

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Registry No. $UO_2(acac)_2$, 18039-69-5; $UO_2(hfa)_2$, 67316-66-9; $U(acac)_4$, 17923-26-1; $U(tfa)_4$, 32627-13-7; $Th(acac)_4$, 17499-48-8; $Zn(acac)_4$, 17501-44-9.

References and Notes

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