with an important bridge stretching character, as it has been proved for the "ν_s(Mo–central oxygen)" mode in the hexamolybdate anion.[14]

Conclusion

In this study of a great number of polyoxo compounds related to the Keggin structure, we have demonstrated that, in most cases, anion–anion interactions of electrostatic type are responsible for a strong increase in the stretching frequencies. These interactions have been correlated with the cation size, since the higher the M–O_d stretching frequencies, the smaller the cation. These interactions vanish when the counterion is large enough to keep the polyanions far apart (e.g., the TBA counterion). A minimal distance of about 6 Å between the external oxygens of adjacent polyanions seems required for neglecting anion–anion interactions.

The solid TBA compounds can be proposed as good models for isolated anions in the crystal lattice and can be used as references. The vibrational techniques are proved to be efficient for detecting and interpreting slight effects difficult to study with crystallographic techniques.

Further work dealing with solvent effect on these compounds is now in progress.

Acknowledgment. The authors wish to thank Prof. J. P. Perchard for helpful discussions concerning electrostatic interactions.

Note Added in Proof. A recent paper (Fuchs, J.; Thiele, A.; Palm, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 789) reports preliminary results about the structure of α-$PW_{12}TBA$ ($V = 8526.3$ Å^3, $Z = 4$): these results agree with our conclusions (see text and Table III).

Registry No. Ia, 12027-12-2; Ie, 75329-24-7; Ik, 59138-97-5; IIIa, 12411-35-7; IIIc, 67954-33-0; IIIk, 81205-59-6; Va, 12026-57-2; Vc, 55624-58-3; Vk, 53749-36-3; Vl, 3844-82-0; VIIb, 83844-89-7; VIIk, 81158-05-6; IXd, 11078-54-9; IXk, 83844-83-1; Xa, 12027-38-2; Xd, 12027-46-2; Xf, 12161-28-3; Xh, 77214-65-4; Xk, 51542-99-5; XIe, 83861-67-0; XIg, 77981-80-7; XIi, 83844-84-2; XIj, 83844-85-3; XIl, 83844-86-4; XIIa, 12207-33-9; XIId, 83844-90-0; XIIk, 83844-87-5; XIVa, 1343-93-7; XIVd, 12026-98-1; XIVk, 53749-37-4; XVc, 78143-04-1; XVk, 83844-88-6.

Supplementary Material Available: Discussion of thermogravimetry experiments and tables of TG results (3 pages). Ordering information is given on any current masthead page.

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Photoelectron Spectroscopy of f-Element Organometallic Complexes. 3. Chloro, Bromo, Methoxy, and Methyl Complexes of Triindenylthorium(IV) and -uranium(IV)

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This paper presents a study of photoelectron spectra of a series of triindenylactinide(IV) complexes containing various σ-bonded ligands. Studies were performed with both He I and He II ionizing sources. The first data on details of the valence electronic structure have been obtained. It is found that the bonding of the ring ligand in indenyl complexes is similar to that found in corresponding cyclopentadienyl complexes even though there are indications of a greater 5f covalency in the former. Along the series of the studied complexes, differences have been found as far as the nature of the σ-bonded ligand is concerned. There is evidence, in $U(ind)_3CH_3$, of a tendency toward ionicity, which can account for the observed band shape associated with the $5f^{-1}$ ionization in its spectrum.

Introduction

Ultraviolet photoelectron (PE) spectroscopy has proven to be an important technique for studying the electronic structure of actinide complexes.[2] It has provided revelant information about perturbations due to actinide valence orbitals on the ligation environment. Various classes of actinide compounds including both organometallic[3,4] and classical coordination[5] complexes have thus far been studied. Complexes of the indenide ligand are of particular interest among actinide organometallics. Their coordination closely resembles that in corresponding cyclopentadienyl complexes even though variations due to the greater steric demand of the ligand and to the involvement in the bonding of electrons mainly localized on the six-membered ring of the indenide anions cannot be excluded a priori. In this paper we report on He I and He II excited PE spectra of the triindenylactinide complexes $An(C_9H_7)_3X$ (An = Th, U) containing various σ-bonded ligands ($X = Cl, Br, OCH_3, CH_3$). Motivation for the study is the almost unique possibility offered by PE spectroscopy utilizing variable photon energies of elucidating the energy ordering of valence molecular orbitals and their atomic compositions. This information, *directly* related to metal–ligand bonding, becomes particularly valuable as the most reliable rationale for he physicochemical properties of present complexes since only *indirect* insight on the bonding properties has thus far been obtained[6] generally from reactivity data.

Experimental Section

The complexes under study were prepared as described elsewhere.[7] They were purified by sublimation in vacuo. Sample manipulations were carried out in a glovebox under inert atmosphere.

Spectra were run on a commercial Perkin-Elmer PS 18 spectrometer modified for He II measurements by including a hollow-cathode discharge lamp giving a high yield of He II photons (Helectros Development). The ionization energy (IE) scale was calibrated by reference to peaks due to admixed inert gases and to He $1s^{-1}$ self-ionization. Qualitative evaluations of band areas were generally precluded by the complexity of the spectral bands. Thus, intensity arguments were used in He I vs. He II comparison only when variations of peak height are clear and unambiguous.

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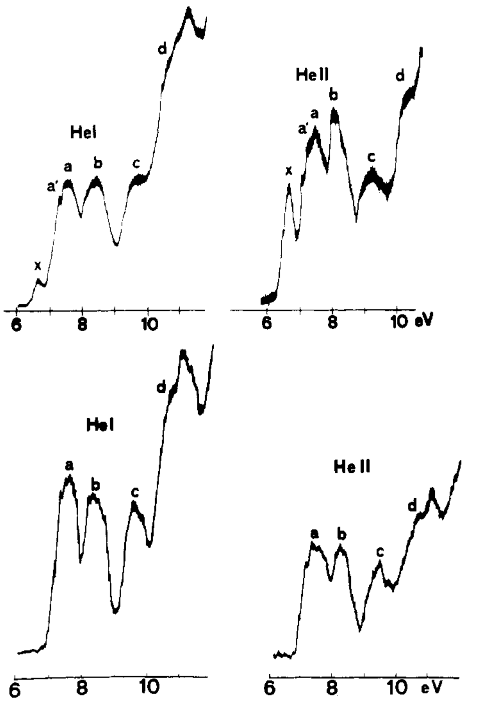

Figure 1. Low-energy region of He I and He II spectra of An(ind)$_3$Cl complexes: top, An = U; bottom, An = Th.

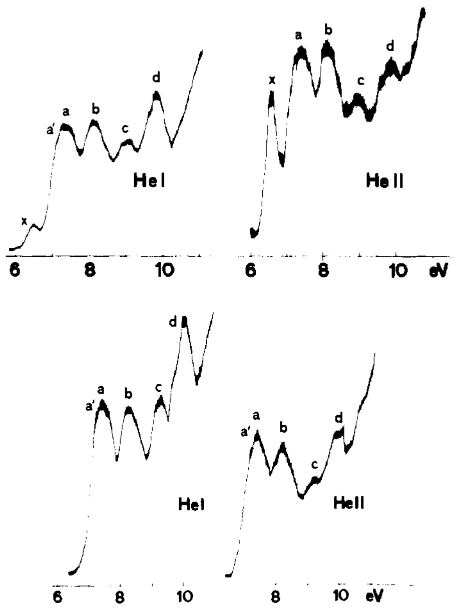

Figure 2. Low-energy region of He I and He II spectra of An(ind)$_3$Br complexes: top, An = U; bottom, An = Th.

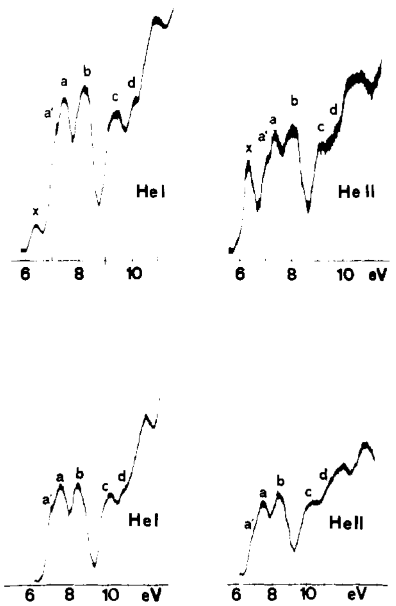

Figure 3. Low-energy region of He I and He II spectra of An(ind)$_3$OCH$_3$ complexes: top, An = U; bottom, An = Th.

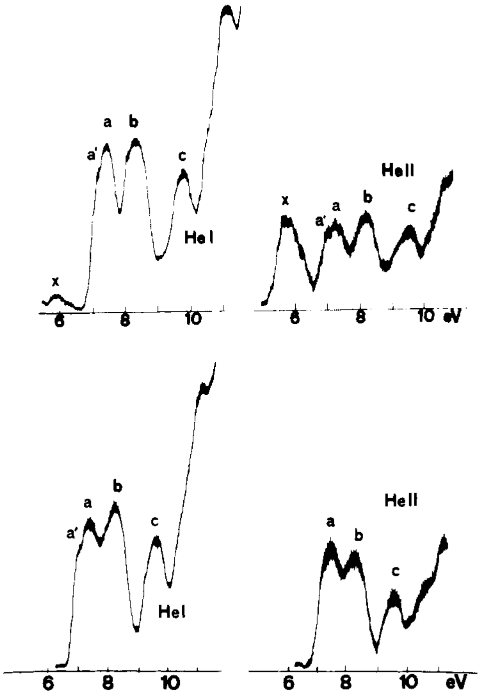

Figure 4. Low-energy region of He I and He II spectra of An(ind)$_3$CH$_3$ complexes: top, An = U; bottom, An = Th.

Results and Discussion

The spectra of all complexes An(C$_9$H$_7$)X (hereafter An(ind)$_3$X) are similar (Figures 1–4). In the case of uranium complexes a low-intensity band (labeled x in the Figures) appears at the onset of their He I spectra. A series of three bands (labeled a–c) follows in all spectra up to 10.0 eV. The band a generally shows a shoulder (a′) on the low-IE side. The spectral pattern in the higher region (>10.0 eV) depends upon the nature of the ligand X. Only when X = Cl, Br, OCH$_3$ is a further band (labeled d) present. In the highest IE region of all the spectra, six other broad bands are present, the last two, beyond 17 eV, being necessarily apparent only in the He II spectra. All these latter bands relate to ionizations of electrons belonging to inner π and to σ molecular orbitals (MOs) of ligand framework. These orbitals are no longer of relevance as far as the metal–ligand bonding is concerned. They will not be the object of further discussion.

Remarkable variations of relative intensities of various bands become evident in spectra excited by the He II radiation. The most noticeable effect concerns the onset band x, which becomes very prominent in He II spectra of all uranium complexes. By contrast the band d suffers a marked intensity falloff (relative to previous bands) in spectra of the chloride and bromide complexes (Figures 1 and 2). A similar effect, with the exception of methoxy complexes (Figure 3), is generally associated with the band c (Figures 1, 2, and 4). Pertinent IE data are reported in Table I.

The assignment of the low-energy bands a–c requires a detailed description of the electronic structure of the simple indenyl anion ligand. Obviously, among indenyl MOs only those that are in relation with the e$_1''$ (D_{5h}) species of the closely related cyclopentadienyl (cp) anion ligand can be of

Table I. Ionization Energy Data and Assignments of Indenyl Complexes Studied

band label	ionization energies, eV								assignt
	UCl	ThCl	UBr	ThBr	$UOCH_3$	$ThOCH_3$	UCH_3	$ThCH_3$	
x	6.63		6.77		6.33		5.70 6.04 6.42		$^2F_{5/2}$
a'	7.07		7.10	7.07	7.05	7.10	7.03	7.02	$2a_2$
a	7.54	7.50	7.60	7.41	7.40	7.40	7.31	7.41	3e
b	8.24	8.35	8.30	8.23	8.16	8.18	8.23	8.11	$1a_1 + 2e$
c	9.61	9.60	9.37	9.27	9.30	9.56	9.80	9.70	1e
d	10.71	10.75	10.00	10.05	10.15	10.10			σ lone pairs

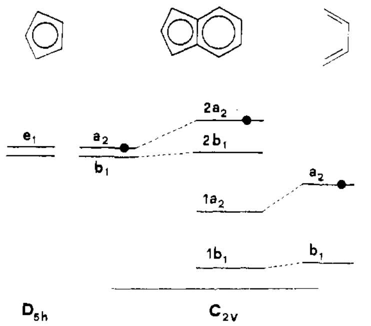

Figure 5. Qualitative description of relevant molecular orbitals in the indenyl anion. Orbitals are filled up to $2a_2$.

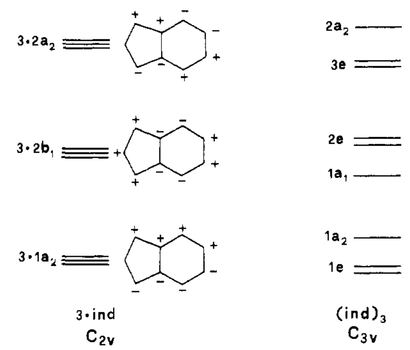

Figure 6. Energy ordering of upper filled MOs in the triindenyl network.

importance in the metal–ligand bonding.[4b] The nature of upper filled pertinent π MOs in the indenyl anion can be gauged by considering the interaction of e_1'' cp MOs with appropriate (on energy and group-overlap grounds) *cis*-butadiene π MOs (Figure 5). In the C_{2v} point group, which is proper for the indenyl anion, this results in the new upper filled $1a_2$, $2a_2$, and $2b_1$ MOs. Their relative energy ordering proposed in the figure agrees well with that indicated by simple Hückel theory as well as by INDO calculations.[8] An interesting peculiarity of the proposed MO scheme is the different nature of the uppermost $2a_2$ and $2b_1$ MOs. In fact, while the wave function related to the former extends over both the six- and the five-membered rings, that of the latter remains almost localized over the cyclopentadienyl ring. These properties will be of relevance as far as the bonding model that we are going to discuss is concerned. Reference to PE data of the π isoelectronic naphthalene[9] suggests that ionizations from the above MOs must be expected in the 7–10-eV region.

Crystal data of $U(ind)_3Cl$[10] have indicated a distorted-tetrahedral structure with η^5-indenyl ligation. Although the bromide complexes seem to be not isomorphous with the above chlorides,[7b] the close similarity of all the present spectra is an indication of analogous structures in the vapor phase. A distorted-tetrahedral structure belonging to the C_{3v} point group will be assumed for all complexes.

In C_{3v} symmetry the relevant indenyl orbitals transform as

$$3a_2 \rightarrow e + a_2 \qquad 3b_1 \rightarrow e + a_1$$

Obviously some off-diagonal mixing between π and more internal σ sets are theoretically allowed because of the low symmetry. However, a wealth of data on various low-symmetry-related complexes unambiguously indicate that relevant ring π orbitals maintain their original character despite the low symmetry.[11]

The energies associated with new symmetry orbitals arising from each set of orginal π indenyl orbitals can be differentiated first by operation of nonbonded interligand interactions. They proved of some relevance in the case of homologous tricyclopentadienyl actinide(IV) complexes.[4] On the basis of interligand group overlaps, the overall energy ordering of upper filled π orbitals over the triindenyl network is as shown in Figure 6.

Further interactions with actinide valence orbitals result in perturbation on these ligand MOs. There were speculations[3,12] as to whether 6d or 5f metal orbitals are of major relevance in the bonding in actinide complexes. Symmetry arguments, however, cannot help in discriminating between the two possibilities, both 6d and 5f sets practically spanning (with the exception of the a_2 species for 6d orbitals) all the representations of the group. The same is true for indenyl MOs. Thus development of a qualitative MO scheme, as used in highly symmetric complexes,[3] seems to be precluded. Nevertheless, variations of relative spectral intensities when a switch is made from He I to He II radiation can be of guidance in detecting, without excluding that of 6d, the involvement of metal 5f electrons in the bonding. It is well-known that the PE cross section of 5f orbitals increases considerably under the He II radiation relative to those of carbon 2p based orbitals as well as halogen *n*p,[4b,c] oxygen 2p,[4d] and metal 6d orbitals.[2] Because of the particular atomic composition of upper filled ligand MOs in the present complexes (vide infra), the increase of relative intensity of a particular PE band at higher wavelength will be a clear indication of some 5f admixture into the corresponding MO.

Turning to a more detailed assignment (Table I), we feel confident in assigning the bands a′ (where resolved), a, and b, respectively, to orbitals $2a_2$, 3e, and $1a_1$ + 2e mainly indenyl (C 2p) based. The variations of relative intensities of these bands provide on passing from He I to He II spectra, however, evidence of relevant metal 5f admixture into the above MOs. It transpires that bands a–b increase in intensity relative to bands that follow in all the He II spectra of the present uranium complexes (Figures 1–4). Such intensity changes become

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much more evident if the spectra are compared with those of corresponding thorium complexes (Figures 1–4). In the latter, in fact, the intensities of bands a–b remain almost unchanged on passing to He-II spectra, thus pointing to a minor involvement of metal 5f orbitals into the metal–ligand(ring) bonding.

In reality, on the basis of group overlaps, we expect important interactions involving metal $5f_{\pm2}$,$5f_{\pm1}$ and ligand 3e and 2e orbitals. In this regard, it is worthy to note that similar interactions have been found to be the major source of bonding in the corresponding complex $U(C_5H_5)_3X$.[2]

In the case of indenyl complexes, however, the interaction involving the $5f_{\pm2}$ and 3e orbitals seems better suited than in cyclopentadienyl complexes. Crystal data of $U(ind)_3Cl$[10] reveal that the six-membered rings of the indenyl moieties are all oriented toward the σ-bonded ligand, thus lying below the equatorial plane[13] through the uranium atom. Therefore, the wave function of the 3e MO (unlike the case for 2e) extends both above and below the equatorial plane. And this is of particular importance as far as the bonding interaction with the $5f_{\pm2}$ metal orbitals is concerned since their particular angular forms mean that they also extend below and above the equatorial plane. Moreover, nodal properties of both mentioned ligand and metal MOs match very well to provide good overlaps. It, hence, may be argued that the energy splitting of $2a_2$ and 3e MOs (bands a′ and a, Table I), not evident in the case of 2e and $1a_1$ (band b), arises because of the stronger bonding properties of the 3e MO. Moreover, we must remind the reader that the band b represents the ionizations of both the 2e and the $1a_1$ MOs (Figure 6, Table I). In reality, both these MOs can interact strongly with $5f_{\pm1}$ and $5f_0$ uranium orbitals. Nevertheless such metal–ligand interactions are less favored on overlap ground than those involving the $5f_{\pm2}$ and 3e orbitals already discussed since the 2e and $1a_1$ MOs are both related to the $2b_1$ orbital in the free indenyl anion (Figure 5) and, hence, almost localized over the five-membered ring. This observation may account for the absence of evident splitting of band b.

The following band c we believe to represent only the ionization of the 1e MO. The PE band related to the remaining $1a_2$ orbital is probably hidden by the more intense structure that follows. In reality, band c is always less intense than band a or b, the (a + b)/c intensity ratio, as measured in the He I spectrum of the methyl complex, where the bands are better resolved (Figure 4), being 3.1/1. This value, given the above assignment, lies close to that expected on occupancy grounds (12/4). It is interesting to inquire about the origin of such a marked 1e–$1a_2$ splitting. The more conceivable explanation can be advanced in terms of destabilization of the 1e MO because of important nonbonded interactions with orbitals of e symmetry localized on the σ-bonded ligands.[14] It turns out that the relative intensity of band c becomes smaller in the He II spectra (Figures 1–4) of chloride and bromide while it stays almost constant in that of the methoxy complex. This trend parallels that of He II cross sections of orbitals over the σ-bonded ligands. It is well-known that Cl 3p[2,11] and Br 4p[11] cross sections become fairly small (relative to C 2p) under He II radiation whereas that of O 2p[15] does not vary remarkably upon switching from He I to He II excitation sources.

The assignment of the following band d in Figures 1–3 does not pose problems. It certainly represents ionization of a nonbonded lone pair over Cl, Br, and OCH_3 ligands since is the band absent in spectra of the methyl complexes (Figure 4). Furthermore the IEs associated to band d (Table II) are almost coincident with the values quoted for corresponding ionizations in the analogous series of $U(cp)_3X$ complexes.[16] Again He I vs He II intensity arguments provide further unequivocal evidence. The band d becomes remarkably smaller in He II spectra of chloride and bromide complexes (Figures 1 and 2) whereas in methoxy complexes no evident variation is observed on changing the exciting radiation (Figure 3). Moreover, the band shifts toward lower IE (Table I) on passing from chlorides to bromides, and this is a well-established trend along the series of homologous halide complexes.[4,11,17]

Table II. Relevant Data for the $5f^{-1}$ Ionization in Various Uranium Complexes

compd	rel He II intens: $5f^{-1}$ band	rel He II intens: ligand bands[a]	half-width of $5f^{-1}$ band,[b] eV	ref
$U(ind)_3Cl$	0.20 (2)[d]	1 (12)	0.30	this work
$U(ind)_3Br$	0.20 (2)	1 (12)	0.35	this work
$U(ind)_3OCH_3$	0.25 (2)	1 (12)	0.46	this work
$U(ind)_3CH_3$	0.45 (2)	1 (12)	0.79	this work
$U(cp)_3Cl$	0.40 (2)	1 (12)	0.35	2
$U(cp)_3BH_4$	0.35 (2)	1 (12)	0.46	2
$U(acac)_4$[c]			0.48	21

[a] Ligand bands refer to ionization from ligand $2a_2$, 3e, $1a_1$ and 2e MOs, in the case of indenyl complexes (Figure 6; bands a–b in the text). In the case of cyclopentadienyl complexes, they represent the $1a_2$, 2e, 1e, and a_1 MOs.[2,4b] [b] Taken from He II spectra. [c] acac = acetylacetonate anion ligand. [d] Values in parentheses are statistical values taken proportional to occupancy.

Finally we comment on the "onset band" x appearing in the spectra of all the present uranium complexes. There is no doubt that it represents final states from the uranium $5f^2$ ground configuration.[2–5,18] The band increases remarkably in intensity relative to ligand bands that follow in the spectra, a behavior peculiar of $5f^{-1}$ ionizations.[3–5] When final-state $5f^1$ structures produced by removal of one electron from the ground state ($J = 4$) of the U(IV) ion are considered, both spin–orbit and ligand field effects must be taken into account. Among them the first has proven to be of major relevance. Literature data[2–5,18] thus far reported on various actinide complexes have indicated that the onset band appearring in their PE spectra must be related to production of the ${}^2F_{5/2}$ ion state. Structures representing the other spin–orbit component have never been observed, first because the statistical probability of reaching the latter final state is very small.[2] Moreover, the expected energy separation ${}^2F_{7/2}$–${}^2F_{5/2}$ ($\Delta E = 7/2\xi_{5f} \simeq 0.7$ eV) results, in any case, in the ${}^2F_{7/2}$ signal to be hidden over the very intense ligand bands that generally follow $5f^{-1}$ structures.

This applies to the present complexes $U(ind)_3X$ when X = Cl, Br, OCH_3. In these cases the onset band x certainly represents the ${}^2F_{5/2}$ state. In reality a cubic ligand field can split the $J = {}^5/_2$ level into E″ and U′ components (into the corresponding double, spinor, group). Nevertheless our spectra do not show evidence of splitting of the band x while the half-width is generally comparable to that measured in PE spectra of other uranium complexes (Table II). Clearly also in present indenyl complexes the ligand field acts as a minor perturbation upon filled 5f subshells. Interestingly, the increase of intensities of 5f signals relative to those due to the following

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(13) The equatorial plane can be defined orthogonal to the C_3 symmetry axis through the uranium atom.

(14) In the present $An(ind)_3X$ complexes, the six-membered rings of the indenyl anions practically surround the σ-bonded ligands. This geometry allows remarkable nonbonded interligand interactions between ring-based MOs and inner orbitals localized on the σ-bonded ligand.

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ligand-centered photoionization processes is less pronounced in present He II spectra than in those of corresponding cyclopentadienyl complexes (Table II). Within the framework of the Gelius model[19] for PE cross sections, this behavior can be understood with the assumption that upper filled ligand π MOs (those responsible for bands a–b) are more admixed with empty U 5f AOs than in cyclopentadienyl complexes.[20] This clearly implies a greater metal–ligand 5f covalence in uranium indenyls.

Turning finally to the methylated complex, we note a greater energy separation between the $5f^{-1}$ band and the following ligand bands (Table I). As noticed before, this may allow detection of some $^{2}F_{7/2}$ structures in the spectrum. Furthermore, the band x appears considerably broader (Table II), a progression being clearly evident on its higher IE side. In addition, the band behaves differently upon varying the ionizing source, the increase an intensity under the He II frequency being much more pronounced than in other U(ind)$_3$X complexes. This indicates a minor admixture of 5f subshells and, thence, a more relevant ionic character of metal–ligand bonding. As far as the progression associated with the band x is concerned, two plausible interpretations can be advanced. First, a vibrational progression could be invoked, the measured interval ($\nu = 2700$ cm^{-1}) being very close to the frequency of the methyl stretching C–H vibration. Nevertheless, such interpretation contrasts with the nonbonding nature of 5f filled subshells inferred from He I vs. He II intensity patterns. Alternatively, the progression may represent split components of $^{2}F_{5/2}$ and $^{2}F_{7/2}$ states. The CH$_3$ group lies, in fact, higher in the spectrochemical series, and hence, in the complex U(ind)$_3$CH$_3$ noncubic components of the ligand field can be relevant in lifting the degeneracy of the $^{2}F_{5/2}$ state, while the stronger ligand field can mix the various components of $J = {}^{5}/_{2}$ and $^{7}/_{2}$ states. Clearly further experimental as well as theoretical works are desirable in this direction and, for instance, PE spectra of U(ind)$_3$CD$_3$ may provide a definitive answer.

Conclusions

This study provides the first direct approach to the electronic structure of indenyl actinide complexes. This is of particular relevance since, thus far, only superficial information on the bonding has been obtained from reactivity data. It transpires that interactions between $5f_{\pm 2}$, $5f_{\pm 1}$ metal orbitals and appropriate symmetry combinations of indenyl orbitals (3e, 2e) are relevant sources of bonding. This observation points to a close analogy with bonding in related cyclopentadienyl complexes even though there is indication that the interaction involving $5f_{\pm 2}$ is better suited, on overlap grounds, in the present indenyl complexes because of the particular angular form of the interacting indenyl-based 3e orbital. Moreover, the intensity changes associated with ionizations of ligand-based MOs in the He II spectra indicate a more relevant involvement of 5f orbitals into the metal–ligand bonding of uranium complexes than in corresponding thorium analogues. Futhermore, if intensity changes associated with $5f^{-1}$ ionizations in the He II spectra of U(ind)$_3$X complexes are compared with those in corresponding cyclopentadienyl complexes, there is indication of a greater 5f covalency in the former. This observation can be related to the minor chemical reactivity of actinide(IV) indenyls.

Interesting information has been obtained about the nature of bonding of the σ-bonded ligand in the present An(ind)$_3$X complexes. There has been evidence of a tendency toward ionicity when X = CH$_3$. This can explain the complexity of the band shape associated with $5f^{-1}$ ionization in U(ind)$_3$CH$_3$.

Finally we would stress that this study reinforces our earlier contention that photoelectron spectroscopy utilizing a variable photon source, probably represents the most powerful tool for investigating the details of the valence electronic structures of actinide complexes. It represents the most suited reference of sophisticated MO calculations while, on a pure experimental basis, the comparison among series of conceivably related complexes can provide information about their relative stability, thus throwing light on their chemistry.

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Registry No. U(C$_9$H$_7$)$_3$Cl, 11082-70-5; Th(C$_9$H$_7$)$_3$Cl, 11133-05-4; U(C$_9$H$_7$)$_3$Br, 57034-56-7; Th(C$_9$H$_7$)$_3$Br, 57034-55-6; U(C$_9$H$_7$)$_3$OCH$_3$, 63643-45-8; Th(C$_9$H$_7$)$_3$OCH$_3$, 63643-44-7; U(C$_9$H$_7$)$_3$CH$_3$, 63643-55-0; Th(C$_9$H$_7$)$_3$CH$_3$, 63643-54-9.

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(19) Gelius, U. "Electron Spectroscopy"; Shirley, D. A., Ed.; North-Holland: Amsterdam, 1972; p 1.

(20) Within the framework of the Gelius[19] model, the wavelength dependence of a cross section of a particular MO depends upon the atomic orbitals that enter the corresponding LCAO. Because of the very large increase of the 5f cross section under the He II wavelength, the admixture of 5f AOs with ligand-based (C 2p in nature) orbitals results in higher intensities of ligand bands under He II photon flux. Clearly the present relative intensity pattern may be the result of anomalously smaller He II cross sections of filled 5f uranium subshells because of admixture with virtual ligand MOs. This possibility, however, must be ruled out in the case of U(ind)$_3$X (X = Cl, Br, OCH$_3$). It should result either in the splitting or in the broadening of band x, at variance with the half-widths found experimentally.

(21) Casarin, M.; Ciliberto, E.; Fragalà, I.; Granozzi, G. *Inorg. Chim. Acta* **1982**, *64*, L247.