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Preliminary communication

PHOTOELECTRON SPECTROSCOPY OF *f*-ELEMENT ORGANOMETALLIC COMPOUNDS

II. TRICYCLOPENTADIENYL DERIVATIVES OF URANIUM(IV) AND THORIUM(IV)*

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Summary

The photoelectron spectra of some cyclopentadienyl derivatives of uranium(IV) and thorium(IV), namely $(C_5H_5)_3ThCl$, $(C_5H_5)_3UCl$, $(C_5H_4CH_3)_3ThCl$, $(C_5H_4CH_3)_3UCl$, $(C_5H_4CH_3)_3UBr$ and $(C_5H_4CH_3)_3UBH_4$, are reported the metal 5*f* ionization has been detected in all the uranium derivative spectra and a simple molecular orbital scheme qualitatively accounts for the number and position of the observed low energy bands.

A study of the photoelectron (PE) spectra of two highly symmetrical dicyclooctatetraenidoactinide(IV)-systems recently provided the first direct information about the highest occupied molecular orbitals of organoactinide compounds [1]. In order to gain further insight into the bonding in such compounds, we are studying the PE-spectra of actinide organometallics of lower point symmetries than D_{8h}, including both ring-substituted actinocenes and tricyclopentadienyl complexes, $Cp_3U^{IV}X$ ($Cp = \eta^5$-C_5H_5 or η^5-$C_5H_4CH_3$).

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We report below some preliminary observations on the PE-spectra of various uranium(IV) and thorium(IV) complexes of the latter type, which involves the largest group of homologous organoactinide systems. Compounds of this class do not have the symmetry requirements which were helpful in explaining the relatively high stability of the actinocenes [2], but the Cp_3MX-systems do als exhibit a remarkable stability.

All the spectra were recorded on a Perkin—Elmer PS 18 PE-spectrometer using a heated inlet probe. The temperatures used are listed in Table 1 together with the measured ionization energies. All spectra were calibrated by reference to the xenon and argon peaks. The high energy region ($IP \geqslant 11$ eV) is practically identical for all compounds studied. The simple two-band structure in this region resembles closely the corresponding patterns shown by other cyclopentadienyl complexes of various symmetries [3,4]. These bands have been ascribed to ligand π and σ ionizations whose energies are too high to substantially contribute to the metal-to-ligand bonding.

TABLE 1

IONIZATION ENERGY DATA (eV) AND WORKING TEMPERATURES (*W.T.* (°C)) RELATIVE TO $(C_5H_5)_3UCl$; $(C_5H_4CH_3)_3UCl$; $(C_5H_4CH_3)_3UBr$; $(C_5H_4CH_3)_3UBH_4$; $(C_5H_5)_3ThCl$ AND $(C_5H_4CH_3)_3ThCl$

$(C_5H_5)_3UCl$	$(C_5H_4CH_3)_3UCl$	$(C_5H_4CH_3)_3UBr$	$(C_5H_4CH_3)_3UBH_4$	$(C_5H_5)_3ThCl$	$(C_5H_4CH_3)_3ThCl$
6.90	7.10	6.95	6.35	—	—
			6.75		
8.00	8.05	8.20	8.10	7.85	7.75
8.50 (8.70)	8.55	8.50	8.45	8.55	8.25
9.20	9.25	9.20	8.85	9.20	8.95
10.40	10.55	9.95	(10.30)	10.55	10.45 (10.65)
12.40	12.10	12.35	11.95	12.55	12.15
13.20	13.15	13.10	12.75	13.40	13.20
16.40	15.95	16.40	15.85	16.50	16.00
W.T. 198	149	178	122	190	195

Representative low energy spectra are shown in Fig. 1. All compounds containing X = Cl exhibit one band between 10.0 and 11.5 eV apparently characteristic of lone pair ionization of the chloride ligand. This assumption is supported by a shift of this band towards lower energy when Cl is replaced by Br, and by its complete absence for X = BH_4 (Fig. 1)..

Between ca. 7.5 and 9.5 eV, ionization from the symmetry-adapted linear combinations of the individual ligand $p\ \pi$-orbitals is expected. Energy matching with some assumed positions of the pure metal orbitals suggests that the e_1-*SO*'s of each Cp-ligand (of local symmetry C_{5v}) would be most suited for the metal-to-ring bonding, and to a lesser extent the empty e_2-*SO*'s. In C_{3v}-symmetry, which seems most appropriate for the complexes under consideration, each set of *SO*'s will give rise to four symmetry-adapted linear combinations transforming like a_1, a_2 and $2 \times e$. The PE spectrum of $(C_5H_5)_3UCl$, as well as those of the other uranium and thorium congeners,

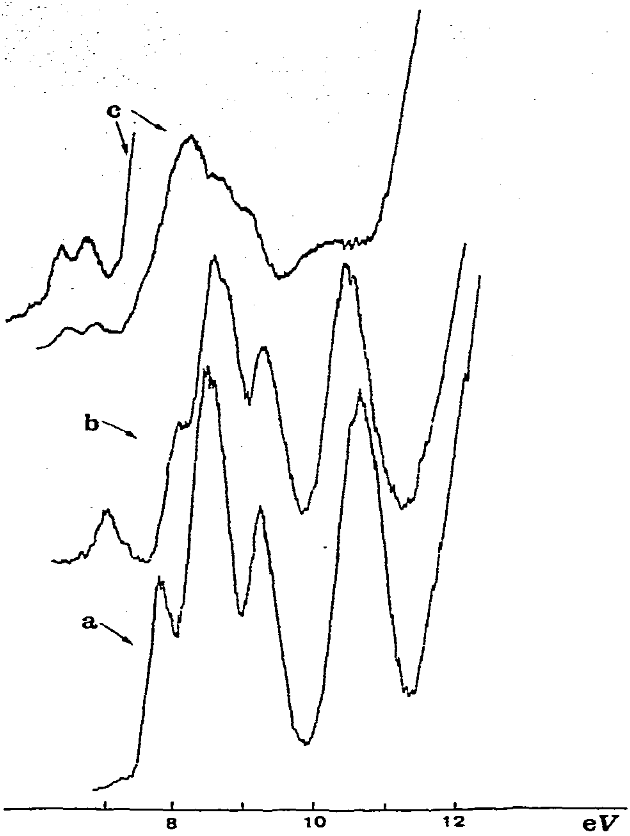

Fig.1. Photoelectron spectra of: (a) $(C_5H_5)_3ThCl$; (b) $(C_5H_5)_3UCl$; (c) $(C_5H_4CH_3)_3UBH_4$. Low energy region.

show at least three well-resolved bands in this region, so that inter-ligand through space and/or metal-ligand through bond interactions must account for energetic splitting of the occupied orbitals.

As the three occupied *p-AO*'s of the halide ligand transform like a_1 and e, it is expected that some interaction between the π-Cp linear combinations and the Cl orbitals of the representation a_1 and e, respectively, will destabilize ring orbitals of either type. In view of the approximate intensity ratio 1:3:2 of the three well resolved ring orbital ionizations, the energetic sequence: $a_1 > a_2 + e^{(1)} > e^{(2)}$ seems likely. The accidental degeneracy of the orbitals a_2 and $e^{(1)}$ appears to be removed in the complex $(C_5H_5)_3UCl$, where the band centered at 8.6 eV shows s shoulder at its high energy side (Fig. 1, Tab. 1). The above energetic sequence is also in accordance with the result of a recent *MO* calculation on the complex $(C_5H_5)_3TiCl$ [4] which suggests a considerable admixture of halide orbitals to the upper filled ring orbitals (up to 20%). Furthermore, the reverse intensity ratio of roughly 3:2:1 observed in the $(C_5H_4CH_3)_3UBH_4$-spectrum (Fig. 1) underlines the specific role played by the halide orbitals in determining the energetic order.

All the uranium complexes show at the onset of their spectra at least one band of rather low intensity which is strongly reminiscent of the weak bands which appear at the onset of the PE-spectra of other organometallic [1,5,6] and coordination compounds [7] of uranium(IV). The absence of this band in all homologous thorium(IV) derivatives, which have the ground configuration [Rn] $5f^0$, suggests strongly that a partial occupation of the $5f$-subshell is essential for the existence of such "onset-bands". It would be premature to attempt to decide whether these bands arise exclusively from direct $5f$-electron ionization or from exchange effects which are common for open shell systems. It is noteworthy in this context that the "f-band" of the complex $(C_5H_4CH_3)_3UBH_4$ is a doublet, and that the position of the "f-band" is most sensitive to the composition of the ligand sphere (ranging from 6.15 eV in uranocene [1] to 7.10 eV in $(C_5H_4CH_3)_3UCl$).

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