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PHOTOELECTRON SPECTROSCOPY OF ACTINIDE ORGANOMETALLIC COMPOUNDS

I. BIS(CYCLOOCTATETRAENE)ACTINIDE(IV) COMPLEXES *

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Summary

The He(I) photoelectron spectra of the antinocene species Th(cot)$_2$ and U(cot)$_2$ (cot = cyclooctatetraene) have been determined. The 5*f* metal ionization has been detected at the onset of the uranocene spectrum. The low ionization energy region of both spectra is discussed in terms of simple qualitative molecular orbital scheme.

The nature of the bonding in the organometallic compounds of the actinide elements has been of interest since their discovery. The stability and the properties of such a type of compound have often been explained by invoking a ligand (π-MO)—metal (*f* orbitals) interaction, but the problem does not lend itself to simple approaches. Various experimental techniques, NMR, UV, IR, Mössbauer spectroscopy and magnetic measurements [1], gave information about the bonding in these compounds.

UV photoelectron spectroscopy, by singling out individual molecular orbitals, throws light on the electronic structure of these substances, and we plan to measure the UV photoelectron spectra of a large number of actinide organo-

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metallics. Currently we are studying the substituted cyclooctatetraene (cot) [2], cyclopentadienyl [3] and indenyl [4] derivatives of uranium(IV) and thorium(IV), but we describe below the photoelectron spectra of Th^{4+} and U^{4+} bis(cyclooctatetraene) derivatives.

Experimental

The $U(cot)_2$ and $Th(cot)_2$ species were prepared by published methods [5] and purified by high vacuum sublimation at 150°C and 165°C respectively. They gave correct elemental analyses and their spectra agreed well with the published data. All manipulations were carried out in a glove box operating under argon. Photoelectron spectra were recorded on a Perkin—Elmer PS18 photoelectron spectrometer using an heated inlet probe. The working temperatures were 177° C for the uranocene and 187°C for the thoracene. Both spectra were calibrated by reference to the xenon and argon peaks.

Results and discussion

The photoelectron spectra of uranocene and thoracene (Fig. 1, 2) show well resolved bands of comparable intensity in the 6.5—8.0 eV and 9.8—10.5 eV region. In the spectrum of $U(cot)_2$ there is also a band of relatively low intensity at 6.15 eV. For both compounds the high IE region consists of two amorphous systems of overlapping bands. These high IE bands resemble the corresponding bands in the spectrum of the cyclooctatetraene ligand [6], although detailed comparison is impossible due to the different molecular symmetries. The details of the low IE region can be explained, through Koopmans approximation, in

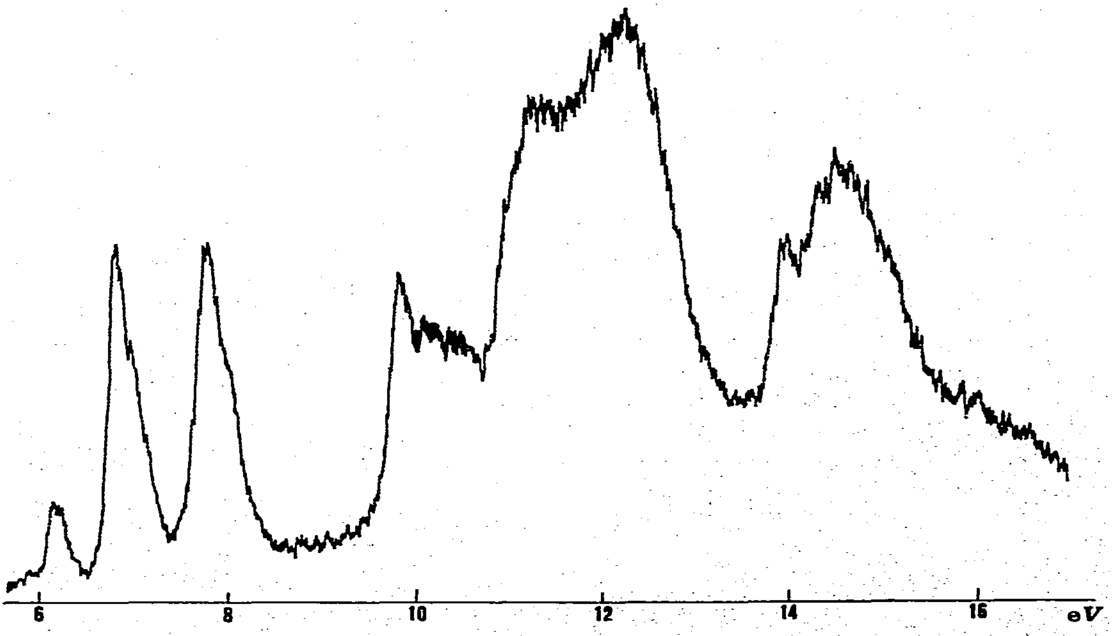

Fig. 1. He(I) photoelectron spectrum of $U(cot)_2$.

terms of a simple MO * model analogous to that originally proposed by Streitweiser et al. in 1968 [7].

Considering first the ligand electronic system, the $C_8H_8^{2-}$ dianion can be considered as an effectively planar aromatic system of D_{8h} symmetry [8]. The eight 2p carbon AO's, the ligand π-system, form a basis for the representations: A_{1u}, E_{1g}, E_{2u}, E_{3g}, B_{2u}.

This ordering is that predicted for the energies of the corresponding MOs by the simple Hückel theory. In view of the amorphous structure in the high IE region and the similarity in this same region between the spectra of actinocenes and the spectrum of the parent cyclooctatetraene, there is little point in considering the σ orthogonal system. The uranocene molecule has a sandwich eclipsed structure with the planes of the two rings parallel. The point group is D_{8h}. This crystal structure found by X-ray diffraction analysis [9] has been assumed for the vapour phase.

Consideration of the non-bonded interactions between the two ligands suggest the possible electronic structure of the $(C_8H_8)_2^{4-}$ framework. The symmetric and antisymmetric combinations of the $C_8H_8^{2-}$ SO's on the D_{8h} point group lead to the orbitals with the transformation characteristics shown in Fig. 3. The SO's arising from the b_{2u} orbital were not considered because they are very high in energy, and cannot contribute significantly to the bonding. The splitting of each original SO leads to a small differentiation between them such that the

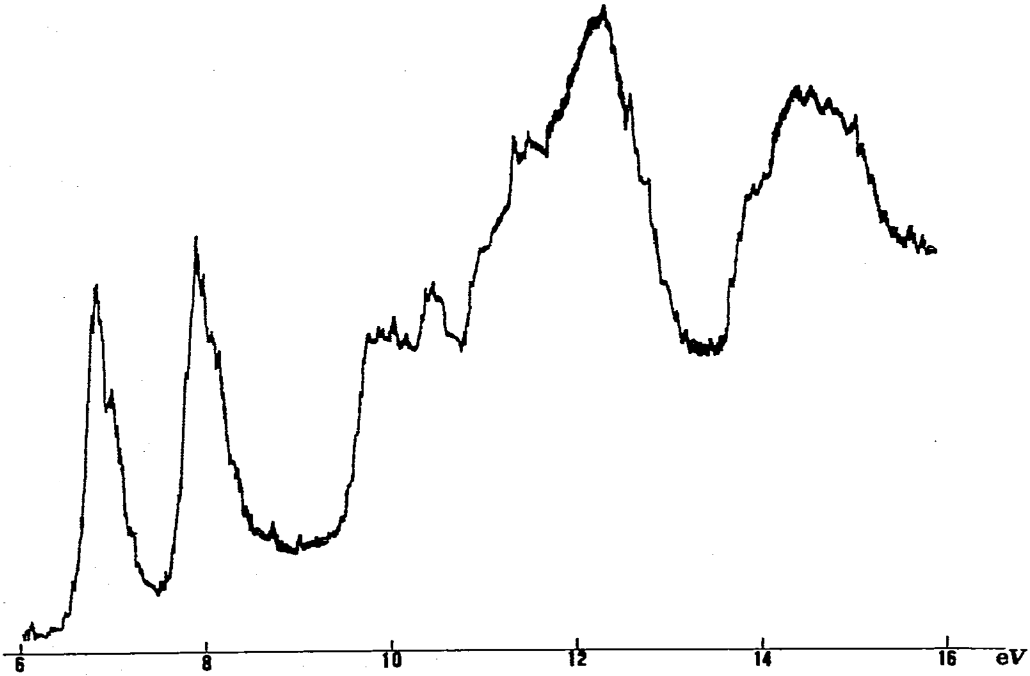

Fig. 2. He(I) photoelectron spectrum of Th(cot)$_2$.

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* MO = molecular orbital; AO = atomic orbital; SO = symmetric orbital.

final ordering of the $(C_8H_8)_2^{3-}$ SO's will not be changed with respect to those of the corresponding SO's of the simple $C_8H_8^{2-}$. The orbital basis set for the actinide elements must include the 5*f*, 6*d*, 7*s* and 7*p* orbitals, but some of these are too high in energy to contribute to the covalent bonding, and only the 5*f* and eventually the 6*d* need to be considered. The transformation properties of the 5*f* orbitals in the D_{8h} point group have been reported [5] and they can be shared with the ligand orbitals in the symmetry permitted combinations.

Energy matching should be favorable for the f_{xyz}, $f_{z(x^2-y^2)}$—e_{2u} and for the $f_{x^2-3y^2}$, $f_{y(3x^2-y^2)}$—e_{3u} interactions. Similarly the relative overlap values computed by Hayes and Edelstein [10] suggest a strong interaction. The resulting qualitative MO scheme is reported in Fig. 3.

The low IE structure of the spectrum of $U(cot)_2$ can be fitted into this scheme and the proposed assignments are listed in Table 1.

The highest filled MO (e_{3u}) corresponds to an orbital essentially metallic in character. The corresponding photoelectron band at the onset of the spectrum agrees well with this interpretation. Its intensity, which on the occupacy considerations should be half that of the second band, is considerably lower (Tab. 1). The cross-section of the *f* orbitals is expected to be smaller than that of the ligand MO's, and similar intensities were observed for *f* ionizations in other

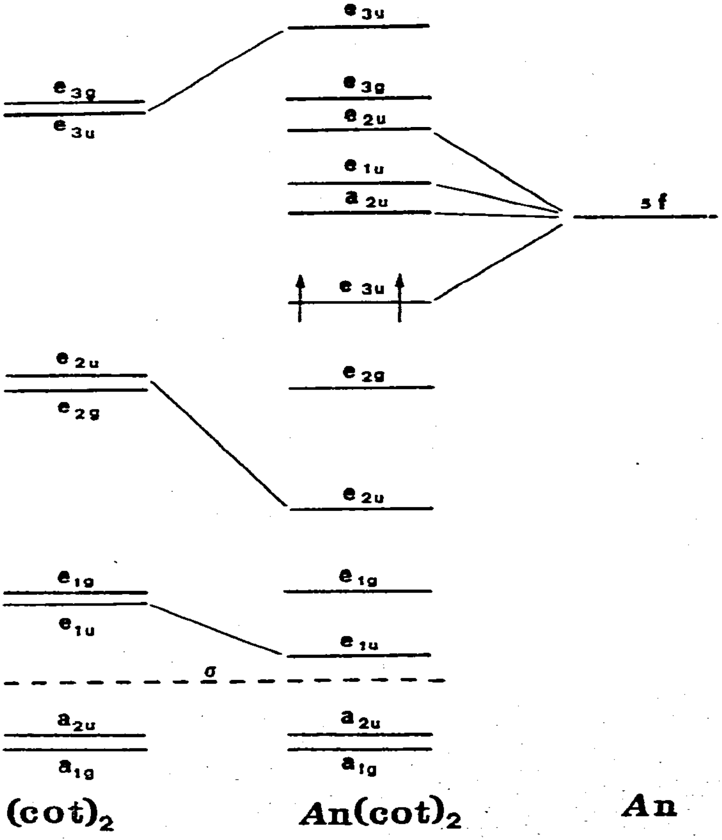

Fig. 3. Qualitative molecular orbital scheme for the actinocenes. The eclipsed (D_{8h}) configuration is assumed.

TABLE 1

IONIZATION ENERGY DATA (eV) AND RELATIVE BAND INTENSITIES FOR $Th(cot)_2$ and $U(cot)_2$ [a]

$Th(cot)_2$		$U(cot)_2$		Assignment
		6.15	[0.23]	e_{3u}
6.75 (6.93)	[1.00]	6.80 (6.95)	[1.00]	e_{2g}
7.85 (7.97)	[1.17]	7.75 (7.87)	[0.94]	e_{2u}
10.00		9.80 10.20		e_{1g} e_{1u}
10.50		10.50		σ
11.55		11.40		
12.35		12.30		
14.10		13.90		
14.60		14.50		

[a] Shoulders are shown in parentheses. The values in square brackets indicate relative band intensities.

organometallic [2—4] or coordination compounds [11] of the actinide elements. The second band relates to the e_{2g} non-bonding MO belonging to the ligand framework and the third to the bonding e_{2u} orbital responsible for the covalent bond between the metal and the ring, which results in a net charge transfer from the ligand to the metal. The shapes of the above bands agree well with this interpretation. The sharp onset of the band at 6.80 indicates a non-bonding nature, while for the third band a half width greater than that of the e_{2g} band indicates some bonding character. The complex profiles on the high IE side are probably due to vibronic (Jahn—Teller) interaction in the ^2E ion states. Similar behaviour was observed in the photoelectron spectra of transition metal metallocenes [12].

This tentative scheme is supported by Hayes—Edelstein empirical calculations and by the observed opposite shift of the NMR methyl and ring hydrogen proton signals on the symmetrical alkyl substituted uranocene [13]. The Mössbauer isomer shift measured in neptunocene [14] also suggests a covalence involving the $f(e_{2u})$ orbital.

The spectrum of the thoracene molecule in the 6—8 eV region shows only two bands of approximately equal intensity whose separation is slightly greater than that in the uranocene spectrum. These two bands can obviously be assigned to e_{2g} and e_{2u} ionizations by analogy with the corresponding bands of the congener U^{4+} derivative. Clearly the $e_{3u}f$ ionization does not appear in the $Th(cot)_2$ spectrum, the Th^{4+} ion having an f^0 formal structure.

The bands present in the $U(cot)_2$ and $Th(cot)_2$ spectra in the 9.5—10.5 eV region display some differences. In the $U(cot)_2$ spectrum a sharp band can be discerned at 9.8 eV as well as two diffused ill-resolved bands centered, respectively, at 10.2 and 10.5 eV. The $Th(cot)_2$ spectrum shows only two diffused bands at 10.0 and 10.5 eV. These bands can be assigned in terms of the qualitative MO scheme outlined above. The $U(cot)_2$ ionizations at 9.8 and 10.2 eV correlate with e_{1g} and e_{1u} MO. The shapes and the intensities of these bands agree well with the characteristics of the corresponding MO's. The same orbitals are in the $Th(cot)_2$ less split, due to the lowering of the metal—ligand interaction.

so that they coalesce to give a unique band at 10.0 eV. The ionization at 10.5 eV probably relates to a ligand σ MO in both U^{4+} and Th^{4+} derivatives. The constant position of this band, on going from the Th(cot)$_2$ to the U(cot)$_2$ supports this interpretation. On the other hand the increased charge density of the ring carbon in the $C_8H_8^{2-}$ dianion suggests the shift of some σ ionization of the neutral C_8H_8ligand to lower energies. This indicates in the uranocene a stronger metal—ring interaction and thus a stronger covalence than in the thoracene.
In this respect the low energy bands, namely the e_{3u}, e_{2g} and e_{2u} bands, require some further comment. Assuming the e_{2g}—e_{2u} splitting to be a measure of the metal—ring interaction, the smaller value in the U(cot)$_2$ spectrum compared with that of Th(cot)$_2$ suggests an increased covalence in the latter compound. This does not agree, however, with the lower e_{1u}—e_{1g} splitting in Th(cot)$_2$. Moreover the more favorable energy matching for the e_{2u}—f_{xyz}, $f_{z(x^2-y^2)}$ interaction in respect to the e_{1u}—f_{xz^2}, f_{yz^2} make unreasonable an opposite trend in the e_{1g}—e_{1u} and e_{2g}—e_{2u} splittings on going from the Th(cot)$_2$ to the U(cot)$_2$. Some bonding interaction between the uranium $6d_{xz}$, $6d_{yz}$ and the ligand e_{2g} SO must be responsible for the observed trend. This interaction, however, still involves the same f metal—π ligand interaction in both Th^{4+} and U^{4+} derivatives.

Careful examination of the relative intensity of the e_{2g} and e_{2u} bands (Fig. 4) reveals an inversion of the intensity ratio on going from Th(cot)$_2$ to the uranium analogue. The reduced intensity of the U(cot)$_2$ e_{2u} band can be attributed to an increase, relative to the thorium parent compound, in the metal f AO of lower cross-section. This indicates an increased covalence in the case of uranium, and thus some additional effect must be invoked to explain the reduced e_{2g}—e_{2u} splitting.

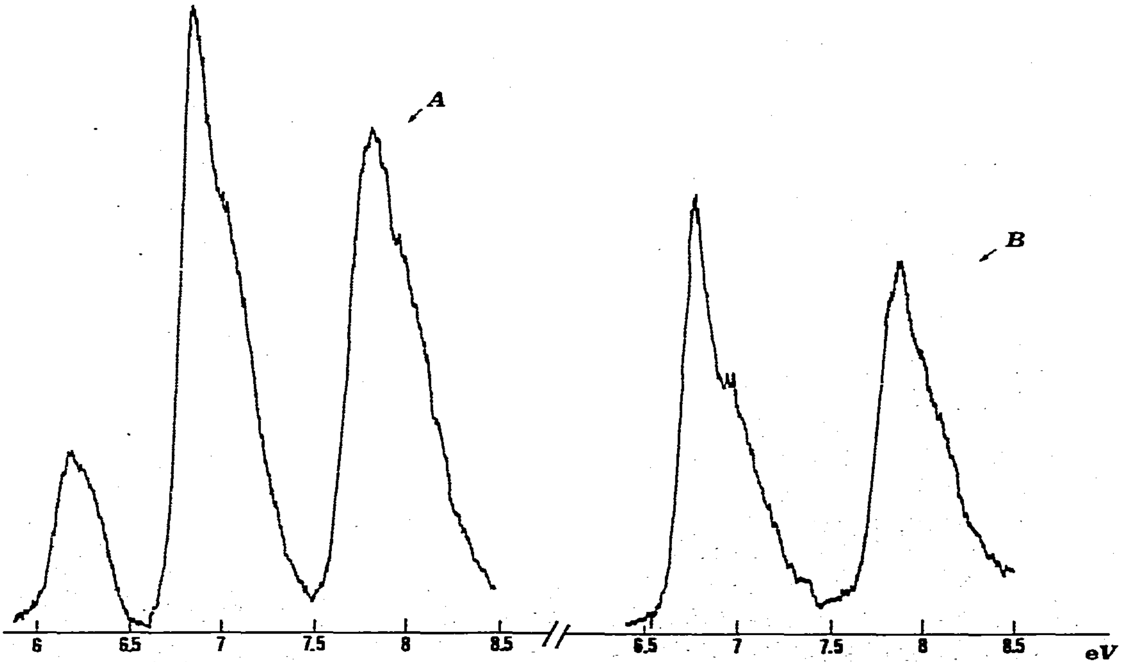

Fig. 4. Expanded scale photoelectron spectra of actinocenes. Low IE region. (A) U(cot)$_2$; (B) Th(cot)$_2$.

X-ray diffraction data indicate a ring—ring distance in the $Th(cot)_2$ higher than in $U(cot)_2$ [9]. The reduced ring—ring interaction in the thoracene molecule destabilizes the ligand non-bonding e_{2g} MO, thereby accounting for the increased e_{2g}—e_{2u} splitting.

The intensity of the e_{3u} f band in the $U(cot)_2$ spectrum also gives information about the covalence of the metal—ring bond. Its intensity, although small, is considerably greater than that for other actinide organometallics, the intensity ratio refered to a π ligand band is 0.25 in $U(cot)_2$ (Tab. 1, Fig. 4) while it is 0.10 or less in cyclopentadienyl or indenyl derivatives [3,4]. This suggests that a back-bonding $f_{x(x^2-3y^2)}, f_{y(3y^2-z^2)}$—$e_{3u}$ combination increases the 5f photoelectron cross-section. Although photoelectron spectra indicate that some role is played by 5f electrons in the metal—ligand bond of the bis(cyclooctatetraene)-actinide(IV), it would be, unwise at present to emphasize the role taken by the symmetry factors in this class of compounds.

Work in progress in this laboratory on other actinide organometallic systems with different symmetries and with different π ligands, should enable more defined analyzes to be made.

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