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Preliminary communication

THE He-I PHOTOELECTRON SPECTRA OF URANOCENE AND THOROCENE

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Summary

The bonding in uranocene and thorocene is discussed in the light of their photoelectron spectra and ionization of 5*f* electrons is identified.

The di-η-cyclooctatetraenylactinide complexes have been studied by various physical methods in order to obtain information on their electronic structure. Streitwieser et al. [1] propose that a source of covalent bonding in uranocene is interaction between the e_2 orbitals of the cyclooctatetraenyl rings and the $f_{\pm 2}$ orbitals of uranium, Mössbauer studies on neptunocene [2] indicate covalency in this compound. ^{1}H NMR studies on uranocene [3] and 1,3,5,7,1′,3′,5′,7′-octamethyluranocene [4] give contact shifts consistent with negative spin-density in cyclooctatetraenyl π-orbitals. Molecular orbital calculations [5] have been carried out which give a bonding model substantially in agreement with that proposed by Streitwieser et al. This theoretical study includes a calculation on the f^2 configuration involving electrostatic, spin-orbit and crystal field interactions, which indicates a ground state for uranocene with $|J_z| = 3$. This gives good agreement with magnetic susceptibility data [2, 5]. Streitwieser et al. [6] simply suggest as a "working hypothesis" that the two *f*-electrons occupy the *f*-orbitals with $l_z = \pm 3$ which is the lowest energy orbital on a crystal field model.

We have measured the He-I photoelectron spectra of uranocene and thorocene. The compounds were prepared by reported methods [1, 6]. The spectra were obtained using a Perkin—Elmer PS 16/18 spectrometer with the sample at temperatures between 150—180°C.

The spectrum of uranocene is given in Fig. 1. That of thorocene is similar but lacks the low energy ionization band observed for uranocene. Vertical ionization energies for both compounds are given in Table 1. If we just consider the cyclooctatetraene π-electrons and the metal valency electrons, we base our assignment

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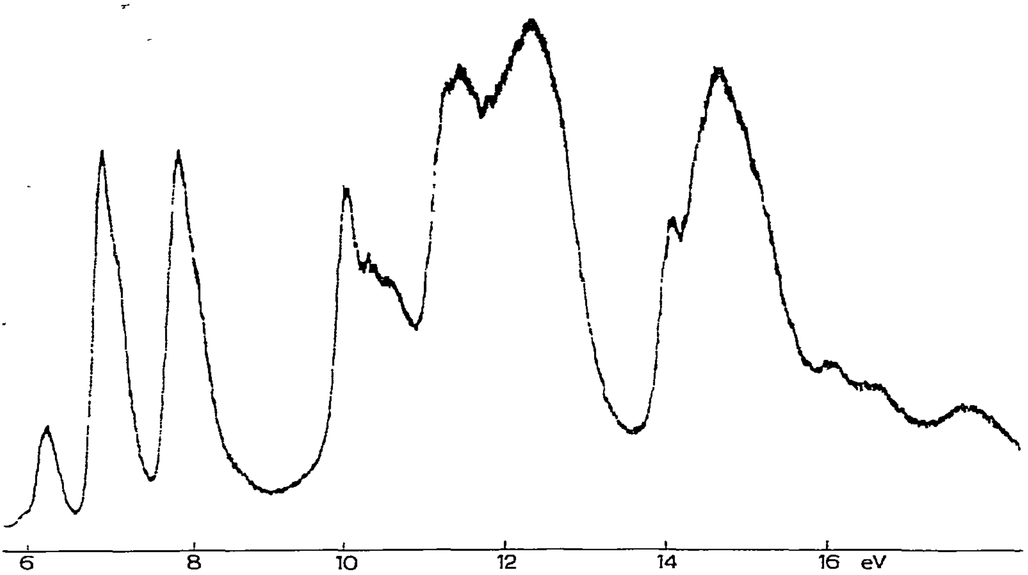

Fig. 1. The photoelectron spectrum of uranocene.

on an electronic configuration $a_{1g}^2 a_{2u}^2 e_{1u}^4 e_{1g}^4 e_{2u}^4 e_{2g}^4 f^n$ where $n = 0$ for thorocene and 2 for uranocene.

The first band (6.2 eV) in the spectrum of uranocene is clearly due to ionization of the f^2 electrons, this band being absent in the spectrum of thorocene which has an f^0 configuration. This band shows no structure and is symmetrical with a half-width of ~0.3 eV. This information does not enable us to choose between the various ground states proposed for uranocene as it seems reasonable on either model that the accessible f^1 ion states would lie close in energy.

Subsequent assignment of the spectra is similar for uranocene and thorocene. The next two bands (6.90 and 7.85 eV (U); 6.79 and 7.91 eV (Th)) have very similar profiles with a sharp leading edge and a shoulder on the higher IE side.

TABLE 1

IONIZATION ENERGIES (eV) OF URANOCENE AND THOROCENE

$(\eta\text{-}C_8H_8)_2U$	$(\eta\text{-}C_8H_8)_2Th$	Assignment
6.20		
6.90	6.79	e_{2g}
7.85	7.91	e_{2u}
9.95	9.90	$e_{1u} + e_{1g}$
10.28	10.14	
10.56	10.65	
11.50	11.48	
12.37	12.32	
14.09	14.12	
14.67	14.65	
16.10	16.17	
16.73	16.74	
17.85	17.91	

They are assigned to ionization from the e_{2g} and e_{2u} orbitals respectively. If we assume that *f*-orbital covalency is greater than either *d*-orbital covalency or ring—ring interaction as is generally accepted [6], ionization from the e_{2u} orbital is expected to occur at higher energy than from the e_{2g} orbital. Perhaps the most striking feature about these two bands is their separation (~0.95 eV). This is greater than that found for other sandwich molecules [7] with identical rings except for $(\eta\text{-}C_5H_5)_2Mg$ and $(\eta\text{-}C_5H_4Me)_2Mg$ [8]. In this latter case however both metal—ring and ring—ring interactions tend to stabilise the e_{1u} orbital. This separation indicates that there is a substantial differential interaction binding one set of e_2 orbitals significantly more than the other.

The next set of bands (9.94 and 10.24 (10.48 (sh)) eV (U), 9.90. 10.14 and 10.65 eV (Th)) are assigned to ionizations from the e_{1g} and e_{1u} orbitals. Most *e* symmetry ionization bands in sandwich compounds show shoulders on the high IE side due to Jahn—Teller distortion in the molecular ion [9], as does the first ionization band of benzene. Thus the structure and intensity of this set of bands is consistent with overlapping ionization bands from e_{1u} and e_{1g} orbitals. The splitting of the e_1 bands is apparently less than the e_2 pair, confirming that the latter are more important in bonding.

Subsequent bands are assigned to ionization from the a_{1g} and a_{2u} orbitals and ionization of the σ-structure of the cyclooctatetraenyl rings. The onset of these complex bands at 11.0 eV is consistent with the interpretation of the PE spectrum of $(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)Ti$ [7]. The first band assigned to σ-structure in cyclooctatetraene occurs at 11.72 eV [10]. The bands assigned to ionization of electrons chiefly localized on the cyclooctatetraenyl ring in $(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)Ti$ occur at 7.62 eV (e_2) and 10.51 eV (e_1) consistent with our assignments for uranocene and thorocene.

The spectra of these cyclooctatetraenyl complexes show striking resemblance to those of other sandwich molecules of the transition metals. The lowest bands are due to ionization of electrons largely localized on the metal with very low ionization energies demonstrating the electron-rich nature of the metal. An ionization energy of 6.2 eV for uranocene which is formally a uranium(IV) compound is comparable with that of a uranium atom (6.08 eV).

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