An Investigation of the Electronic Structure of Bis(η-cyclo-octatetraene)-actinoids by Helium-(I) and -(II) Photoelectron Spectroscopy †

By **John P. Clark** and **Jennifer C. Green**,* Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

The He(I) and He(II) photoelectron spectra of $[M(\eta\text{-}C_8H_8)_2]$ (M = Th and U) have been recorded. Ionization of 5*f* electrons is identified and their relative cross-section is shown to increase when the ionizing radiation is changed from He(I) to He(II). The bonding in these molecules is discussed and it is proposed that the major stabilizing interaction is between the ring $e_2(\pi)$ and the metal 6*d* orbitals. Significant *f*-orbital covalency is also demonstrated.

SEVERAL attempts have been made to test the proposition of Streitwieser and Muller-Westerhoff [3] that a source of covalent bonding in $[U(\eta\text{-}C_8H_8)_2]$ is interaction between the *ungerade* combination of the e_2 orbitals of the cyclo-octatetraene rings and the $5f_{\pm 2}$ orbitals of uranium. The structure and bonding of bis(η-cyclo-octatetraene)actinoids has been reviewed recently,[4] with the conclusion that the nature and extent of *f*-orbital participation in the bonding of these complexes has never been satisfactorily established. Molecular-orbital (m.o.) calculations [5] give a bonding model substantially in agreement with Streitwieser's proposition, but uranium 6*d* orbitals were not included in the basis set. The various physical methods used to study the electronic structure of bis(η-cyclo-octatetraene)actinoid complexes provide evidence of covalency but are unable to pinpoint its origin. These include Mössbauer studies [6] on $[Np(\eta\text{-}C_8H_8)_2]$ and ^1H n.m.r. studies [7] on $[U(\eta\text{-}C_8H_8)_2]$ and its 1,3,5,7,1′,3′,5′,7′-octamethyl derivative.[8] Magnetic-susceptibility data [5,6] on $[M(\eta\text{-}C_8H_8)_2]$ (M = U, Np, or Pu) were interpreted by Hayes and Edelstein [5] in terms of ground states with $|J_z| = 3$(U), $\frac{5}{2}$(Np), and 0(Pu).

We have recorded the photoelectron (p.e.) spectra of $[M(\eta\text{-}C_8H_8)_2]$ (M = U and Th) in the expectation that this is a more discriminating method for the investigation of the electronic structure of these molecules.

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† Part of this work has been communicated previously.[1] Similar He(I) spectra have been reported independently.[2]

[1] J. P. Clark and J. C. Green, *J. Organometallic Chem.*, 1976, **112**, C14.

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[3] A. Streitwieser and U. Muller-Westerhoff, *J. Amer. Chem. Soc.*, 1968, **90**, 7364.

[4] E. C. Baker, G. W. Halstead, and K. N. Raymond, *Structure and Bonding*, 1976, **25**, 23.

[5] R. G. Hayes and N. Edelstein, *J. Amer. Chem. Soc.*, 1972, **94**, 8688.

[6] D. G. Karraker, J. A. Syone, E. R. Jones, and N. Edelstein, *J. Amer. Chem. Soc.*, 1970, **92**, 4841.

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EXPERIMENTAL

The complexes $[Th(\eta\text{-}C_8H_8)_2]$ [9] and $[U(\eta\text{-}C_8H_8)_2]$ [10] were prepared by previously reported routes. The p.e. spectra were obtained using a Perkin-Elmer PS16/18 spectrometer, and a Helectros hollow-cathode discharge lamp operating at 200 mA.

RESULTS AND DISCUSSION

The complexes are assumed to have D_{8h} symmetry in the vapour phase which is the symmetry found by crystal studies.[9,11] Symmetry treatment of the bonding is straightforward. For the purposes of assigning the low ionization-energy (i.e.) region of the p.e. spectra, we considered an atomic basis set of the 16 carbon p_π orbitals of the two rings and the metal 7*s*, 6*d*, and 5*f* orbitals. The metal 7*p* orbitals were neglected as they were assumed to lie too high in energy to contribute significantly to the bonding. Simple Hückel m.o. theory and consideration of ring–ring interaction gave a level scheme for the ring-symmetry-adapted m.o. of $a_{1g} < a_{2u} \ll e_{1u} < e_{1g} \ll e_{2g} < e_{2u} \ll e_{3u} < e_{3g} \ll b_{1g} < b_{2u}$. The b_{1g} and b_{2u} levels cannot interact with any of the metal orbitals and may be neglected. Otherwise only the e_{3g} ring orbitals are forbidden on symmetry grounds from interacting with our atomic basis set. The metal *f* orbitals were assumed to lie between the e_2 and e_3 levels giving a configuration for these sandwich molecules of $a_{1g}{}^2a_{2u}{}^2(e_{1g}e_{2u})^8(e_{2g}e_{2u})^8f^n$ ($n = 0$ for Th and $n = 2$ for U). At this stage we make no assumption about the relative ordering of the *e* sets of orbitals or about the f^2 configuration.

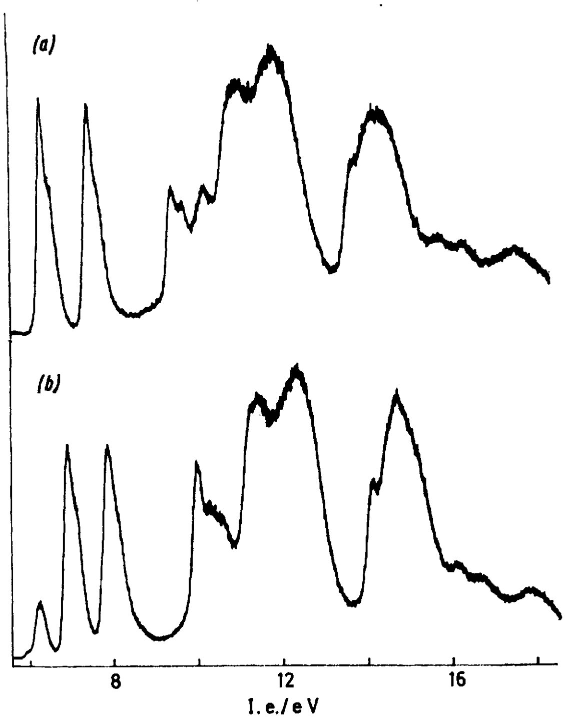

FIGURE 1 He(I) p.e. spectra of (*a*) $[Th(\eta\text{-}C_8H_8)_2]$ and (*b*) $[U(\eta\text{-}C_8H_8)_2]$

He(I) *Spectrum of* $[Th(\eta\text{-}C_8H_8)_2]$ *and* $[U(\eta\text{-}C_8H_8)_2]$.—The He(I) spectra for $[M(\eta\text{-}C_8H_8)_2]$ (M = Th and U) are given in Figure 1 and the ionization energies are reported in Table 1. We now proceed to an assignment of these spectra based on the electron configuration given above.

TABLE 1

Vertical ionization energies (eV)

$[Th(\eta\text{-}C_8H_8)_2]$	$[U(\eta\text{-}C_8H_8)_2]$	Assignment
	6.20	f^n
6.79	6.90	e_{2u}
7.91	7.85	e_{2g}
9.90	9.95	
10.14	10.28	e_{1u}, e_{1g}
10.65	10.56	
11.48	11.50	
12.32	12.37	a_{1g}, a_{2u} and σ structure of the ring
14.12	14.09	
14.65	14.67	
16.17	16.10	
16.74	16.73	
17.91	17.85	

The p.e. spectrum of $[U(\eta\text{-}C_8H_8)_2]$ had a band at low i.e. (6.2 eV) * which was clearly absent in the spectrum of $[Th(\eta\text{-}C_8H_8)_2]$. This is assigned to ionization of the f^2 configuration. This band showed no structure, was symmetrical, and had a half-width of 0.3 eV.

Subsequent assignment of the spectra is similar for the two molecules. The next two bands [6.90 and 7.85 eV (U); 6.79 and 7.91 eV (Th)] had very similar profiles with a sharp leading edge and a shoulder on the higher i.e. side. These profiles are similar to those obtained by ionizations from *e* orbitals in benzene and in other sandwich compounds and are due to Jahn–Teller distortion of the molecular ions. These bands are therefore assigned to ionization from the e_{2u} and e_{2g} orbitals. Their separation decreased from $[Th(\eta\text{-}C_8H_8)_2]$ (1.12 eV) to $[U(\eta\text{-}C_8H_8)_2]$ (0.95 eV). The bands were slightly broader in $[U(\eta\text{-}C_8H_8)_2]$ than $[Th(\eta\text{-}C_8H_8)_2]$: the widths at half-weight for the lower and higher i.e. bands were 0.41 and 0.47 eV (U) and 0.37 and 0.41 eV (Th). Ionization from the e_2 orbital of $[Ti(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_8)]$ occurs at 7.62 eV.[12]

The next set of bands [9.95, 10.28, and 10.56 eV (U) and 9.90, 10.14, and 10.65 eV (Th)] are assigned to ionizations from the e_1 orbitals. The three distinct features are compatible with overlapping e_{1g} and e_{1u} ionizations; for example these bands in the p.e. spectrum of $[Fe(\eta\text{-}C_5H_5)_2]$ show three distinct features. The splitting pattern was not clearly defined for $[U(\eta\text{-}C_8H_8)_2]$ but for $[Th(\eta\text{-}C_8H_8)_2]$ the e_{1g} and e_{1u} splitting may be taken as 0.75 eV. The assignment of these bands as e_1

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

[9] A. Streitwieser and N. Yoshida, *J. Amer. Chem. Soc.*, 1969, **91**, 7528.

[10] A. Streitwieser, U. Muller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morrell, K. O. Hodgson, and C. A. Harmon, *J. Amer. Chem. Soc.*, 1973, **95**, 8644.

[11] A. Zalkin and K. N. Raymond, *J. Amer. Chem. Soc.*, 1969, **91**, 5667; A. Avdeef, K. N. Raymond, K. O. Hodgson, and A. Zalkin, *Inorg. Chem.*, 1972, **11**, 1083.

[12] S. Evans, J. C. Green, S. E. Jackson, and B. Higginson *J.C.S. Dalton*, 1974, 304.

is consistent with the interpretation of the p.e. spectrum of [Ti(η-C_5H_5)(η-C_8H_8)] [12] where the ionizations assigned to the e_1 orbitals of the C_8 ring occur at 10.51 eV.

Subsequent bands can be assigned to ionizations from the a_{1g} and a_{2u} orbitals, and orbitals associated with the σ structure of the ring. The onset of these complex bands at 11.0 eV is consistent with the interpretation of the p.e. spectrum of [Ti(η-C_5H_5)(η-C_8H_8)].[12] The first band assigned to σ structure in cyclo-octatetraene occurs at 11.72 eV.[13] It is worth noting that the profile of these bands is very reminiscent of that of bis(η-benzene) complexes which in turn resembles that of benzene itself. The spectrum of cyclo-octatetraene however is substantially different in this region. This is not unexpected in view of the differing stereochemistries of the free and bound ligand.

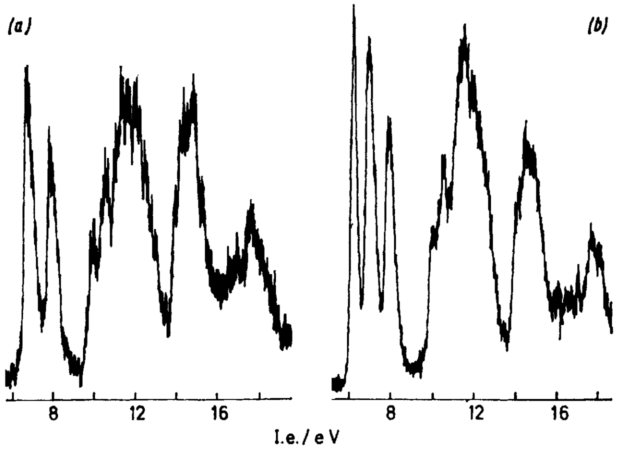

FIGURE 2 He(II) p.e. spectra of (*a*) [Th(η-C_8H_8)$_2$] and (*b*) [U(η-C_8H_8)$_2$]

He(II) *Spectra of* [Th(η-C_8H_8)$_2$] *and* [U(η-C_8H_8)$_2$].—The He(II) p.e. spectra enable us to make a more detailed assignment of the e_2 ionization bands. The low i.e. regions of these spectra are shown in Figure 2 and the relative intensities of the first three bands of [U(η-C_8H_8)$_2$] and the first two bands of [Th(η-C_8H_8)$_2$] are given in Table 2 for both the He(I) and He(II) spectra. The first band in the spectrum of [U(η-C_8H_8)$_2$] underwent a dramatic increase in intensity. From this we conclude that the ionization cross-section for U 5*f* orbitals increases relative to carbon on changing from He(I) to He(II) radiation.*

TABLE 2

Intensity ratios of f^n, e_{2u}, and e_{2g} ionization bands for He(I) and He(II) ionizing radiation

	[Th(η-C_8H_8)$_2$]		[U(η-C_8H_8)$_2$]		
	e_{2u}	e_{2g}	f^n	e_{2u}	e_{2g}
He(I)	1 :	1.1	0.2 :	1 :	1.25
He(II)	1.2 :	1	1 :	1.27 :	1

The relative intensities of the e_2 bands were also changed by the higher-energy exciting radiation, the lower e_2 band increasing in area relative to the higher one in both complexes. This suggests that the m.o.s from which they arise differ in their atomic-orbital constitution as is expected from the difference in symmetry properties of the two orbitals. The e_{2u} m.o. has a possible contribution from metal 5$f_{\pm 2}$ orbitals whereas the e_{2g} orbital may contain metal 6$d_{\pm 2}$ orbitals. No experimental information exists on the relative ionization cross-sections of 6*d* orbitals. It has been observed experimentally [14] that the He(II) : He(I) intensity ratio for metal *d* orbitals relative to that for carbon in a series of complexes of Cr, Mo, and W is Cr $\gg$ Mo $>$ W, that is decreasing as the number of modes in the atomic wavefunction increases. The value for W is approximately unity. A similar trend is observed in ' lone-pair ' *p* halogen ionizations. Extrapolating from the Group 6A metals to uranium we expect little change in the U 6*d* ionization cross-section relative to carbon on changing from He(I) to He(II) ionization, whereas from the He(II) p.e. spectrum of [U(η-C_8H_8)$_2$] it is obvious that the ionization cross-section for 5*f* orbitals increases. Calculations based on a plane-wave model for the ejected electron support this view.[15] Thus we must assign the band with the larger He(II) intensity to ionization from the orbital with the actinoid 5*f* contribution, *i.e.* the e_{2u} orbital. The e_2 band with the *lower* i.e. is assigned to the e_{2u} ionization and the band with the ***higher*** i.e. to the e_{2g} ionization. This assignment differs from that given in our preliminary communication.[1]

If we are bold and assume that the He(II) : He(I) cross-section ratio for 6*d* orbitals is the same as that for carbon *p* orbitals, and that the first band of [U(η-C_8H_8)$_2$] arises from orbitals purely metal *f* in character, we may calculate the percentage *f* character in the e_{2u} orbital by comparing the relative increase in its area with the relative increase in the area of the band at 6.20 eV. The value obtained is 25%, but the figure must be treated with reservation due to the simplicity of the calculation. Although the second e_1 band showed an apparent increase in intensity relative to the first on passing from He(I) to the He(II) radiation, we feel that the resolution of the bands in this region is insufficient to draw any conclusion as to the assignment of these bands.

The Nature of the Bonding in these Complexes.—Now that the p.e. spectra of the complexes have been assigned it is appropriate to relate them to the bonding of the molecules. It is most probable that the energy levels are in the same order as their ionization energies. Although it is possible that Koopmans' theorem may break down, it is unlikely that the approximations involved will lead to inversion of e_{2g} and e_{2u} levels. Differential relaxation for these orbitals, which are both

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* A similar increase in intensity occurs for the 5*f* electrons in [U(BH_4)$_4$] (R. Egdell, personal communication).

[13] C. Batich, P. Bischof, and E. Heilbronner, *J. Electron Spectroscopy*, 1973, **1**, 333.

[14] B. R. Higginson, D. R. Lloyd, P. Burroughs, D. M. Gibson, and A. F. Orchard, *J.C.S. Faraday II*, 1973, 1659.

[15] R. Edgell, personal communication.

largely localized on carbon, is expected to be small. We therefore propose the m.o. ordering shown in Figure 3. The m.o. ordering $e_{2u} > e_{2g}$ is the most novel feature of this scheme and will be discussed further.

This ordering would be expected to result from ring–ring interaction alone. However, it is improbable that this interaction could be strong enough to produce a splitting of *ca.* 1 eV. Crystal studies [11] show that the rings are 3.847 Å apart in [U(η-C_8H_8)$_2$] and 4.007 Å in [Th(η-C_8H_8)$_2$], and at this distance the overlap integral between p_π orbitals on the two rings is very small (*ca.* 0.08). To a first approximation, ring–ring interaction for e_1 and e_2 orbitals will be the same, but the spectral evidence suggests that the e_{2u}–e_{2g} separation is greater than the e_{1u}–e_{1g}. Also we have clear evidence of metal–ligand interaction in the e_{2u} orbital. This latter, if it were the *only* metal–ligand interaction, would cause the e_{2u}–e_{2g} separation to be *less* than the e_{1u}–e_{1g}. Therefore the e_{2u} interaction cannot be the only metal–ligand interaction occurring in the e_1 and e_2 orbitals.

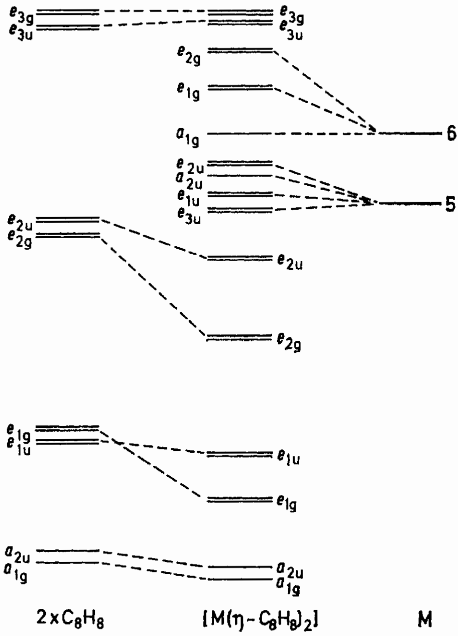

FIGURE 3 M.o. scheme for bis(η-cyclo-octatetraene)actinoids

There remains obviously the conclusion that covalent interaction between the ring e_2 orbitals and actinoid 6*d* orbitals is the major source of bonding in these sandwich molecules. From the intensity data we may also conclude that there is significant covalent interaction between the ring e_2 orbitals and the actinoid 5*f* orbitals. As Streitweiser has pointed out, this stabilizing force is unique for *f*-block transition elements, and may be crucial for determining the properties of these complexes.

This interpretation makes intelligible the trends from [Th(η-C_8H_8)$_2$] to [U(η-C_8H_8)$_2$], *i.e.* the increased e_{2u}–e_{2g} splitting and the increase in the $e_{2g} : e_{2u}$ He(I) intensity ratio. Both these facts lead directly to the suggestion that the ring e_{2u} $f_{\pm 2}$ mixing is greater for [U(η-C_8H_8)$_2$] than for [Th(η-C_8H_8)$_2$]. The increase in nuclear charge from thorium to uranium brings about a contraction and lowering in energy of the *f* orbitals, making them more suitable for bonding in [U(η-C_8H_8)$_2$]. The increase in bandwidth could also be attributed to a greater bonding character for [U(η-C_8H_8)$_2$], but might also be caused by exchange interaction with the unpaired *f* electrons.

In *d*-block sandwich compounds with the electron configuration $e_2{}^4a_1{}^1$ both $^3E_2$ and $^1E_1$ ion states have been observed in the p.e. spectra.[12] This was not the case for [Ti(η-C_5H_5)(η-C_8H_8)] showing a higher degree of localization of the e_2 orbital on the C_8 ring than for smaller rings. No splitting in the e_2 bands is observed for [U(η-C_8H_8)$_2$], but the broadening of these bands relative to [Th(η-C_8H_8)$_2$] may be attributed to the exchange interaction.

Figure 3 also suggests the ordering $e_{1u} > e_{1g}$, but as mentioned above there is no experimental evidence for this. It is proposed by analogy with the e_2 assignments.

Unfortunately the p.e. spectrum does little to elucidate the nature of the ground state of [U(η-C_8H_8)$_2$]. If we assume a $^3A_{2u}$ ground state which results from the configuration $f_{\pm 3}{}^2$, on ionization we have as accessible ion states $^2E_{3u}$ which is split by spin–orbit coupling into two states with $J_z = \frac{5}{2}$ and $\frac{7}{2}$. The separation of these multiplet components is $3\zeta_f$, where ζ_f is the one-electron spin–orbit coupling constant for the metal *f* shell. The value of ζ_f for U^{4+} has been estimated as 0.2 eV.[16] On this model we predict two bands of separation 0.6 eV arising from ionization of the f^2 configuration. We must therefore consider the possibility of a band due to ionization of the f^2 configuration lying under the e_{2u} ionization. We reject this as unlikely because the intensity ratios for the e_{2u} and e_{2g} bands for [U(η-C_8H_8)$_2$] are so similar to those of [Th(η-C_8H_8)$_2$], where there is no *f*-ionization band, in both the He(I) and the He(II) spectra. The spectral evidence is therefore against a $^3A_{2u}$ ground state for [U(η-C_8H_8)$_2$] as is also the magnetic evidence.

Hayes and Edelstein [5] successfully interpreted the magnetic evidence on the basis of a calculation involving ligand-field effects, electron–electron repulsion, and spin–orbit coupling. Given that all these interactions are of the same order of magnitude for [U(η-C_8H_8)$_2$], no simple approach can predict the result of ionizing the f^2 configuration. Further work is clearly desirable.

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[16] R. McLaughlin, *J. Chem. Phys.*, 1962, **36**, 2699.