Journal of Organometallic Chemistry, 212 (1981) 329—340
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SOME PHOTOELECTRON STUDIES ON *f*-BLOCK METAL CYCLOPENTADIENYL COMPLEXES

JENNIFER C. GREEN, M. RUTH KELLY, JUDITH A. LONG
Inorganic Chemistry, Laboratory, South Parks Road, Oxford 0X1 3QR (Great Britain)

BASIL KANELLAKOPULOS
Kernforschungszentrum, Karlsruhe (Germany)

and PAUL I.W. YARROW
School of Molecular Sciences, University of Sussex, Brighton (Great Britain)

(Received December 22nd, 1980)

Summary

He-I and He-II photoelectron spectra have been obtained for $Ln(\eta\text{-}C_5H_4Me)_3$ where Ln = Pr, Dy; $An(\eta\text{-}C_5H_5)_4$ where An = Th, U; $(An(\eta\text{-}C_5H_5)_2Cl_2]$ where Ln = Y, Gd; $U(\eta\text{-}C_5Me_5)_2Cl_2$ and $U(\eta\text{-}C_5H_5)_3(OC_4H_8)$ and He-II spectra for $An(\eta\text{-}C_5H_5)_3Cl$ where An = Th, U; and $U(\eta\text{-}C_5H_4Me)_3Cl$. The spectra are assigned with the aid of qualitative molecular orbital schemes. Ionizations of the *f*-electrons are identified for the actinide complexes but not for the lanthanide complexes. The 5*f* ionization bands show no structure. Relative intensity changes with photon energy in the photoelectron spectra of the actinide complexes are interpreted in terms of *f*-orbital covalency in these compounds. No such evidence is found for the lanthanide cyclopentadienyls. The order of ligand ionization energies in metal cyclopentadienyl halides is discussed in terms of the charge distribution in these molecules.

There have been several previous reports on the photoelectron (PE) spectra of organoactinide complexes. Compounds studied include $An(\eta\text{-}C_8H_8)_2$ [1,2,3] and $An(\eta\text{-}C_5H_5)_3X$ [4] where An = Th and U and X = Cl, Br, or BH_4. Investigations of the frequency dependence of the spectra [2,5] have shown that the relative intensity of *f*-shell ionization increases substantially when the ionizing radiation is changed from He-I to He-II. For uranocene and thoracene Clark and Green [2] proposed that molecular orbitals with metal *f*-orbital contributions should also show an intensity increase on changing the ionizing radiation, and using this premise concluded an ionization energy ordering $e_{2u} < e_{2g}$.

The majority of previous studies have shown only a single band for ionization of the $5f^2$ configuration [1—5]. An exception to this is the spectrum for $U(\eta\text{-}C_5H_5)_3BH_4$ [4]. Related work on electron spectroscopy of lanthanide compounds in the solid state has shown complex spectral patterns for the ionization of the various f^n configurations [6]. These patterns agree well with the predictions of Cox [7]. However, no gas phase UV-PE spectra have been reported for lanthanide compounds.

The present work describes the study of the He-I and He-II spectra of $An(\eta\text{-}C_5H_5)_4$ (An = Th, U), which is possibly a system of sufficient symmetry to use the intensity variation described above as an aid in assigning the spectra. The volatile compound $U(\eta\text{-}C_5H_5)_3 \cdot THF$ enables a study of ionization from a $5f^3$ configuration. The compounds $Ln(\eta\text{-}C_5H_4Me)_3$ (Ln = Pr, Dy) are chosen as examples of analagous lanthanide compounds from the first and second half of the lanthanide series. Various metal cyclopentadienyl chlorides have also been studied to enable a comparison between *f*- and *d*-block compounds to be carried out.

Results and discussion

The photoelectron spectra obtained are shown in Figs. 1—3 and ionization energy data given in Tables 1, 3 and 4. All cyclopentadienyl complexes show a broad band in the region of 11—15 eV that may be assigned to ionization of the lowest lying ring π-orbital and to ionizations of orbitals connected with the σ-structure of the rings. When a cyclopentadienyl group carries a methyl substituent, this band shows a low energy shoulder. Higher energy bands are largely carbon 2*s* in character. These bands are common to all the spectra and will not be discussed further.

$An(\eta\text{-}C_5H_5)_4$

The PE spectra of $Th(\eta\text{-}C_5H_5)_4$ and $U(\eta\text{-}C_5H_5)_4$ (see Fig. 1 and Table 1) are very similar except for an additional band in the spectrum of the uranium compound at low ionization energy. This band shows a substantial increase in relative intensity on increasing the photon energy and so can be assigned to ionization of the f^2 electrons. Three bands are found for both compounds in the region 7—9.5 eV; by analogy with other cyclopentadienyl compounds of actinides and transition metals [4,9,10], these may be assigned to ionization of cyclopentadienyl e_1 orbitals.

The structure of $U(\eta\text{-}C_5H_5)_4$ has been established by X-ray diffraction [11] to consist of four *pentahapto*-cyclopentadienyl rings tetrahedrally bound to the metal atom. In a crystal the individual molecules have S_4 point symmetry. If the metal ring axis were assumed to be an infinite axis of rotation, as has proved a good approximation for transition metal sandwich compounds [12], the molecules would have T_d symmetry. The valence electronic structure in T_d symmetry can be given as

$$1a_1^2, 1t_1^6, 1e^4, 1t_2^6, 2t_1^6, f^n$$

(with no level ordering implied) where only the π-electrons of the cyclopentadienyl rings are considered, and $n = 0$ for Th and $n = 2$ for U. The $1e_1$, $1t_2$ and

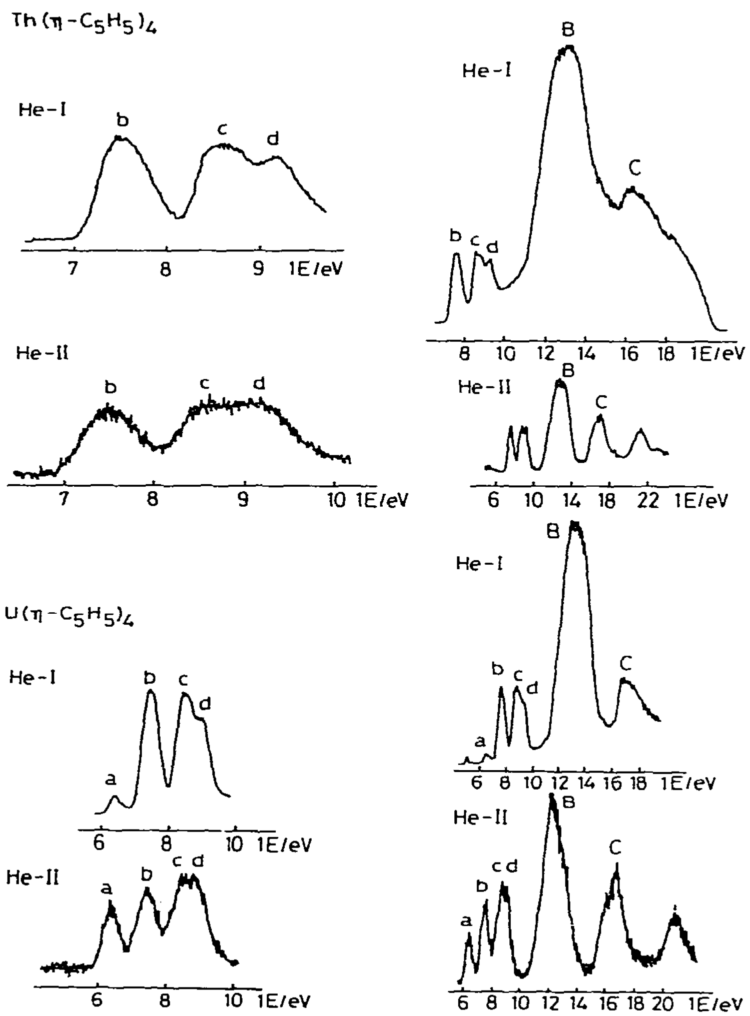

Fig. 1. PE spectra of Th(η-C_5H_5)$_4$ and U(η-C_5H_5)$_4$.

$2t_1$ molecular orbitals (MO) are all likely to have substantial ring e_1 character and will be associated with the three bands in the region 7—9.5 eV. Possible contributions to these from metal orbitals are shown in Table 2. We may move towards a more detailed assignment by considering the He-I and He-II intensity patterns (see Table 1). Bands c and d overlap extensively so it is not possible to assess separate intensities for them, but from the different band profiles of the He-I and He-II spectra, it does appear that band d increases in intensity as the photon energy is increased. From the observations on U(η-C_8H_8)$_2$ and Th(η-C_8H_8)$_2$, this would suggest that it has higher *f* character. The intensity ratios of b : c + d are similar for U(η-C_5H_5)$_4$ and Th(η-C_5H_5)$_4$ and in both cases c + d is relatively more intense in the He-II spectra. Moreover the actual intensity ratios lie closer to the value expected for a t : t + e assignment (1 : 1.67) than for e : t + t assignment (1 : 3). These values assume that the intensities are

TABLE 1

VERTICAL IONIZATION ENERGIES (eV) AND BAND INTENSITIES OF ACITINIDE TETRACYCLOPENTADIENYLS

Band	$U(\eta\text{-}C_5H_5)_4$			$Th(\eta\text{-}C_5H_5)_4$		
	I.E.	He-I int.	He-II int.	I.E.	He-I int.	He-II int.
a	6.34	0.11	0.62			
b	7.39	1.0	1.0	7.49	1.0	1.0
c	8.53	1.6	2.2	8.60	1.5	2.0
d	8.97			9.17		
B	12.65	18.4	13.6	13.21	15.9	11.7
C	16.27	8.1	11.9	16.09	5.9	9.4

roughly proportional to orbital degeneracies, which, for the bis-cyclooctatetraenyl complexes is a reasonable approximation. Several assignments are compatible with the assumption that b must arise from ionization of a *t* orbital. These are

	b	c	d
i)	t_1	e	t_2
ii)	t_2	e	t_1
iii)	t_1	t_2	e
iv)	t_2	t_1	e

Assignments iii and iv are only compatible with the intensity increase of d as interpreted above if the actual lowering of symmetry in the complex is sufficient to allow the metal *f* orbitals to mix with the ligand *e* set. As the t_2 ligand set is able to overlap with both *d* and *f* orbitals on the metal atom, it is reasonable to suppose that the t_2 MO are lower in energy than the t_1 MO and electrons ionized from the t_2 MO (assuming Koopmans' theorem) have a higher ionization potential. For this reason assignment i is preferable to assignment ii.

Extended Hückel MO calculations have been carried out on a $(C_5H_5)_4$ set with distances obtained for the ligands in the $U(\eta\text{-}C_5H_5)_4$ crystal structure. This gave a spread of 0.6 eV for the e_1-derived energy levels. A second calculation assuming C_5 symmetry for the rings, S_4 symmetry overall and average C—C and C—centroid distances from the structure mentioned above gave a spread in

TABLE 2

TRANSFORMATION PEOPERTIES OF *d* AND *f* ORBITALS IN T_d AND S_4 SYMMETRY

d	*f*	T_d		S_4
$d_{x^2-y^2}, d_{z^2}$		e	$\longrightarrow$	$a + b$
	f_{xyz}	a_1	$\longrightarrow$	a
	$f_{x(z^2-y^2)}$ $f_{y(z^2-x^2)}$ $f_{z(x^2-y^2)}$	t_1	$\longrightarrow$	$a + e$
$d_{xy} d_{xz} d_{yz}$	$f_{x^3}\ f_{y^3}\ f_{z^3}$	t_2	$\longrightarrow$	$b + e$

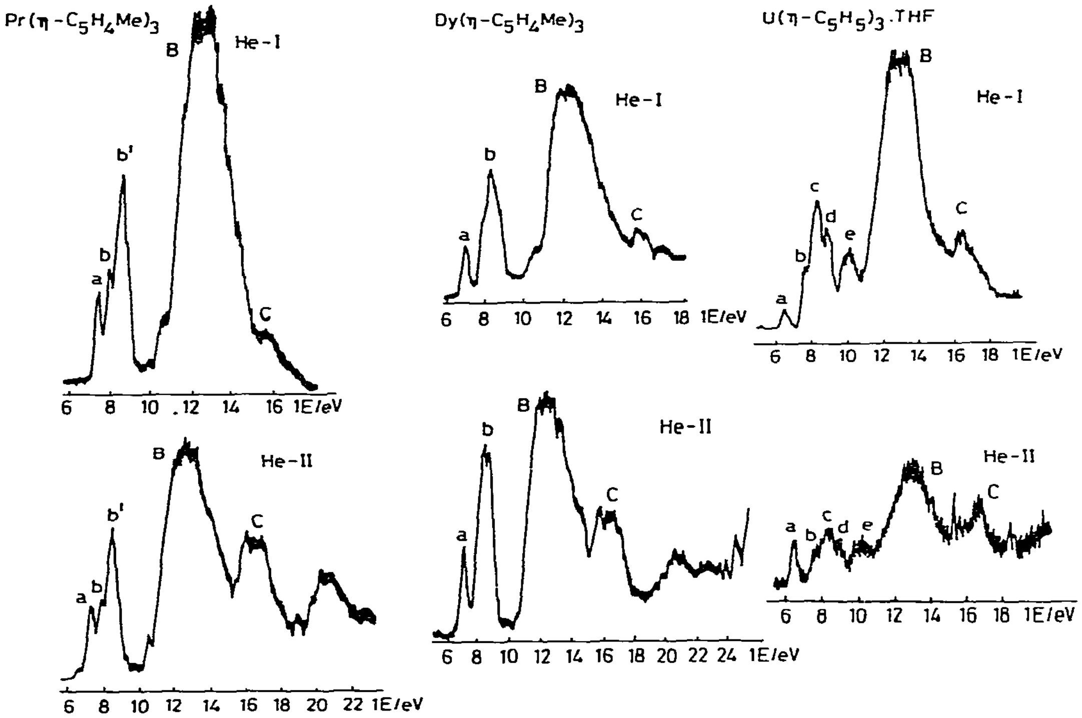

Fig. 2. PE spectra of $Pr(\eta\text{-}C_5H_4Me)_3$, $Dy(\eta\text{-}C_5H_4Me)_3$ and $U(\eta\text{-}C_5H_5)_3 \cdot THF$.

orbital energies of 0.27 eV. Both these values are significantly less than the spread in ionization energies obtained spectroscopically, and suggest that it is ligand—metal interaction that is primarily responsible for the observed splitting pattern of the cyclopentadienyl e_1 levels.

$Ln(\eta\text{-}C_5H_4Me)_3$

The He-I and He-II spectra of $Pr(\eta\text{-}C_5H_4Me)_3$ and $Dy(\eta\text{-}C_5H_4Me)_3$ are shown in Fig. 2 and vertical ionization energies given in Table 3. The first two bands

TABLE 3

VERTICAL IONIZATION ENERGIES (eV) AND BAND INTENSITIES OF $Dy(\eta\text{-}C_5H_4Me)_3$, $Pr(\eta\text{-}C_5H_4Me)_3$ AND $U(\eta\text{-}C_5H_5)_3 \cdot THF$

Band	$Dy(\eta\text{-}C_5H_4Me)_3$			$Pr(\eta\text{-}C_5H_4Me)_3$		
	I.E.	He-I int.	He-II int.	I.E.	He-I int.	He-II int.
a	7.06	1.0	1.0	7.28	1.0	1.0
b	8.39	5.6	4.8	7.86	1.1	1.0
b'				8.41	4.4	3.8
B	10.55			10.53		
	12.22			12.45		
C	15.99			15.88		

of the spectra occur between 7 and 8.5 eV: these are assigned to ionization from the cyclopentadienyl e_1 orbitals.

In assigning the spectra of the tris-cyclopentadienyl lanthanides, it is assumed that a free Ln(η-$C_5H_4Me)_3$ molecule has D_{3h} symmetry with the centres of the three cyclopentadienyl rings at the vertices of an equilateral triangle containing the rare earth atom at its centre. Crystallographic studies [13,14] show that in the solid state the configuration is C_{3v}; intermolecular interaction maximizes the number of electrostatic interactions consistent with the metal ionic radius.

In D_{3h} symmetry the e_1 orbitals transform as $a_2' + a_2'' + e' + e''$. The a_2' orbital is expected to be highest in energy on the basis of unfavourable ligand—ligand interactions. In the He-I spectrum of Dy(η-$C_5H_4Me)_3$ there are two bands that may be assigned to these levels, at 7.06 and 8.30 eV in the approximate intensity ratio of 1 : 5.6 as shown in Table 3. The first band is therefore assigned to ionization from the a_2' orbital, whilst the second band may be attributed to the a_2'', e' and e'' orbitals. In the spectrum of Pr(η-$C_5H_4Me)_3$ the second band is split with a shoulder appearing on the low energy side at 7.86 eV. The bands are approximately in the ratio 1 : 1 : 4. This shoulder is assigned to the a_2'' orbital.

It is interesting to note that the first band of Dy(η-$C_5H_4Me)_3$ occurs 0.22 eV lower than that of Pr(η-$C_5H_4Me)_3$. This is probably a consequence of increasing ligand—ligand repulsion as the metal ion becomes smaller. These observations are in agreement with appearance potentials found from mass spectral studies of the tris-cyclopentadienyl lanthanides [15,16].

A comparison of the He-I spectra with the He-II spectra shows that the relative intensities of bands remains almost constant as shown in Table 3. This is in direct contrast to the spectra of the tetrakis-cyclopentadienyl actinides discussed above, and would suggest very little *f* orbital covalency in the lanthanide complexes.

Furthermore there is no evidence at all of a band anywhere in either the He-I or He-II spectra that could be attributed to ionization of the *f* electrons. Calculations in the ionization cross section of Pr^{3+} have been performed [17] and these predict a 25 : 1 He-II : He-I intensity ratio for the 4*f* orbitals, compared to a 15 : 1 ratio for 5*f* orbitals in U^{3+}. However the He-I ionization cross section for 4*f* orbitals is considerably less than that for 5*f* orbitals, so it is reasonable that 4*f* ionizations may remain undetected in the He-II spectra. In addition, as one progresses along the lanthanide series, although the number of *f* electrons increases, their individual cross-sections decrease as a result of the lanthanide contraction. Calculations [17] predict the intensities of *f*-ionization bands in the spectra of U^{III} and Pr^{III} compounds to be approximately in the ratio 6 : 1. By the time the third transition series has been reached the U^{III} 5*f* : Hf^{III} 4*f* ratio has increased to about 130 : 1, and experimental evidence is in good agreement with this [5]. There is thus very little chance of detecting 4*f* ionizations in compounds of the later lanthanides. Im the case of Pr(η-$C_5H_4Me)_3$ studied here, it is possible that the *f*-ionization band is obscured by other bands in the spectrum.

$U(\eta\text{-}C_5H_5)_3 \cdot THF$

Although this compound is reported to sublime unchanged [18], it was found that, at the temperatures required to obtain reasonable counts for a spectrum some decomposition did take place. This affected the quality of the spectra that we could obtain for this compound (see Fig. 2 and Table 3).

The bands between 7.5 and 9 eV are assigned to the cyclopentadienyl $e_1 p$ orbitals. The band at 10.03 eV arises from ionization of the oxygen lone pair of tetrahydrofuran. This is a slightly higher ionization energy than that found in free tetrahydrofuran, but this may be due to the effect of donation from the oxygen atom in complex formation. The band has approximately the same relative intensity in both He-I and He-II spectra as expected for an oxygen-localized p-ionization.

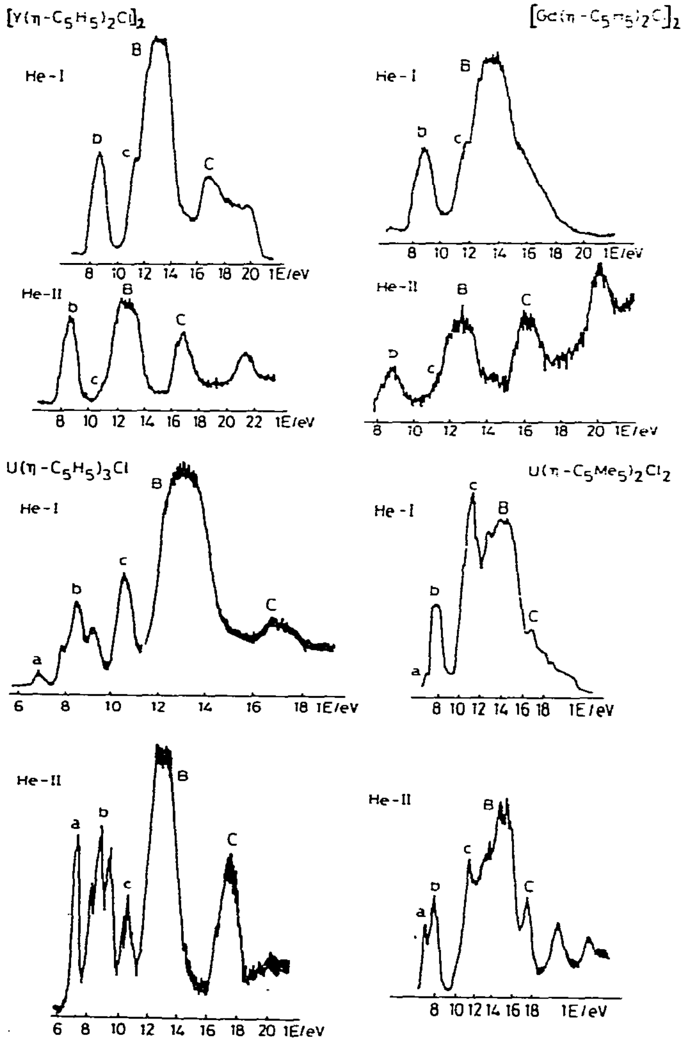

Fig. 3. PE spectra of $[Y(\eta\text{-}C_5H_5)_2Cl]_2$, $[Gd(\eta\text{-}C_5H_5)_2Cl]_2$, $U(\eta\text{-}C_5H_5)_3Cl$ and $U(\eta\text{-}C_5Me_5)_2Cl_2$.

TABLE 4

VERTICAL IONIZATION ENERGIES (eV) AND BAND INTENSITIES FOR LANTHANIDE AND ACTINIDE CYCLOPENTADIENYL HALIDES

Band	$U(\eta\text{-}C_5H_5)_3Cl$	$U(\eta\text{-}C_5H_4Me)_3Cl$	$Th(\eta\text{-}C_5H_5)_3Cl$	$U(\eta\text{-}C_5H_5)_3Cl$		$[Y(\eta\text{-}C_5H_5)_2Cl]_2$	$[Gd(\eta\text{-}C_5H_5)_2Cl]_2$	$U(\eta\text{-}C_5Me_5)_2Cl_2$
				He-I int.	He-II int			
a	7.01	6.91	—	0.09	1.0			6.96
b	7.99	7.92	8.02			(8.22)	8.59	7.59
	8.56	8.32	8.61	1.5	3.6	8.62		8.01
	9.20	8.95	9.31					
c	10.48	10.41	10.74	1.0	0.2	11.31	11.58	10.99
B	12.91	12.76	13.08	10	10	12.84	12.77	13.55
C	17.20	16.09	17.23			16.75		16.51

The low I.E. band at 6.43 eV increases in relative intensity on going from He-I to He-II radiation, so can be assigned to ionization from the f^3 configuration. It is a symmetrical band with no apparent splitting and a width at half height of 0.5 eV. The ground term of the f^3 configuration is $^4I_{9/2}$. Ionization from this gives rise to the final states $^3H_4$, $^3H_5$ and $^3F_2$. The relative probability of producing these states by photoionization has been calculated [19] for an intermediate coupling situation and is given as 2.137 : 0.187 : 0.612, respectively. The $^3H_5$ state is presumably too low in intensity to be readily observed but the $^3F_2$ state, which should lie ca. 0.5 eV above the $^3H_4$ state [20], should be detectable in a good quality spectrum. Unfortunately the high signal to noise ratio that we obtained precludes any definite conclusion as to its presence or absence.

$(Ln(\eta\text{-}C_5H_5)_2Cl)_2$

Though these compounds are dimeric in the solid state [21,22], the gas phase structure is less certain. The ytterbium compound has been shown to retain its dimeric structure in the gas phase [23]. The spectra of the yttrium and gadolinium compounds are very similar (see Fig. 3 and Table 4). Both have a band between 8 and 9 eV that may be assigned to ionizations from the cyclopentadienyl e_1 orbitals. The second broad band between 11 and 14 eV is due to higher cyclopentadienyl ionizations as discussed above. The shoulder on the low I.E. edge of this band is probably due to ionizations from the chlorine orbitals as it is not apparent in the He-II spectrum, and the C 2*p* : Cl 3*p* ionization cross-section ratio is known to increase substantially with photon energy [24]. No evidence of *f*-orbital ionization was found in the spectra of the gadolinium compound.

$An(\eta\text{-}C_5H_4R)_3Cl$

The He-I spectra of $An(\eta\text{-}C_5H_5)_3Cl$ and $An(\eta\text{-}C_5H_4Me)_3Cl$, where An = Th and U, have been reported previously. Our He-II spectra (see Fig. 3 and Table 4) confirm the previous assignment, namely the band ca. 7 eV in the uranium compounds to *f* ionization, the bands between 7.5 and 9.5 eV to cyclopentadienyl e_1 ionizations and that at ca. 10.5 eV, which shows a substantial intensity drop in the He-II spectra, to chlorine ionizations. Our I.E. agree well with those reported, expected that for the *f* ionization we find the methylated complex $U(\eta\text{-}C_5H_4Me)Cl$ has a lower ionisation energy than the unsubstituted $U(\eta\text{-}C_5H_5)_3Cl$, a trend that would be predicted from the known inductive effect of the methyl group.

$U(\eta\text{-}C_5Me_5)_2Cl_2$

The bis-cyclopentadienylactinide dihalides provide analogues of the bis-cyclopentadienyl transition metal dihalides which have been extensively studied by photoelectron spectroscopy [25]. The PE spectrum of the uranium compound is shown in Fig. 3 and ionization energy data given in Table 4. The lowest ionization is that of the *f* electrons at just below 7 eV followed by cyclopentadienyl e_1 ionizations centred round 7.8 eV. The halogen *p* ionizations occur as a shoulder on the main band at 10.99 eV.

The uranium compound resembles the Group IVa bis-cyclopentadienylmetal

TABLE 5

VERTICAL IONIZATION ENERGIES (eV) FOR e_1 ORBITALS IN METAL CYCLOPENTADIENYL COMPLEXES

Compound	I.E. Range
$M(\eta\text{-}C_5H_5)_2$ [a]	8.40—10.33
$U(\eta\text{-}C_5H_5)_3 \cdot THF$	7.58— 8.73
$U(\eta\text{-}C_5H_5)_4$	7.48— 9.17
$Th(\eta\text{-}C_5H_5)_4$	7.40— 9.00
$Pr(\eta\text{-}C_5H_4Me)_3$	7.28— 8.41
$Dy(\eta\text{-}C_5H_4)_3$	7.06— 8.39

[a] M is a first row transition metal.

dichlorides more than the Group VIa analogues in that the halogen electrons ionize at a higher energy than the cyclopentadienyl e_1 ionizations. It is also the case that the chemistry of the uranium compound bears close analogy with those of zirconium and hafnium [26].

Trends in group ionization energies

In Table 5 we summarize characteristic ionization energies for metal cyclopentadienyl and metal cyclopentadienyl chloride complexes.

For the binary metal cyclopentadienyl complexes, the ionization energies of the ring e_1 orbitals decrease as the ionic character of the complexes increases. This trend can be readily interpreted in that the more ionic the character of the complex, the greater the negative charge on the cyclopentadienyl rings and the lower the ionization energies of the orbitals. Alternatively if the e_1 orbital is involved in forming a covalent bond, the electrons occupying it will be delocalized onto the metal and are consequently more difficult to ionize.

A similar trend exists for the e_1 cyclopentadienyl ionizations in the metal cyclopentadienyl halides, the e_1 ionization energy being lowered as the electropositive nature increases. Chloride lone pair ionizations, however, show an opposite trend. With very electropositive metals and compounds of presumed high ionic character such as those formed by the lanthanides and actinides, the

TABLE 6

VERTICAL IONIZATION ENERGIES (eV) OF SOME CYCLOPENTADIENYLCHLORIDE COMPLEXES OF *d*- AND *f*-BLOCK METALS

Compound	Cl *p*	$(\eta\text{-}C_5H_5)\ e_1$
$V(\eta\text{-}C_5H_5)_2Cl$	8.29	9.47, 9.81
$Mo(\eta\text{-}C_5H_4Me)_2Cl_2$	8.73, 8.92	9.70, 10.24, 10.57
$Ti(\eta\text{-}C_5H_5)_2Cl_2$	10.24, 10.65, 11.12	8.46, 8.87, 9.07
$Zr(\eta\text{-}C_5H_5)_2Cl_2$	10.45, 11.12, 11.33	8.6
$Hf(\eta\text{-}C_5H_5)_2Cl_2$	10.60, 11.32, 11.60	8.87, 9.30
$U(\eta\text{-}C_5H_5)_3Cl$	10.48	7.99, 8.56, 9.20
$Th(\eta\text{-}C_5H_5)_3Cl$	10.74	8.02, 8.61, 9.31
$U(\eta\text{-}C_5Me_5)_2Cl_2$	10.99	7.59, 8.01
$[Y(\eta\text{-}C_5H_5)_2Cl]_2$	11.31	8.22, 8.62
$[Gd(\eta\text{-}C_5H_5)_2Cl]_2$	11.58	8.59

chlorine lone pair ionizations are high (ca. 11.5 eV), whereas, with the more covalent transition metal compounds such as $Mo(\eta\text{-}C_5H_4Me)_2Cl_2$, they are below those of the cyclopentadienyl e_1 ionizations.

These trends may be rationalized in terms of a simple charge flow model for these molecules. Let us suppose, for a first approximation, that the charge on a chloride ligand is insensitive to a change of metal. In this case the ionization energy of a chloride lone pair of electrons will be a function of the charge on neighbouring atoms and largely dominated by the charge on the metal. Changes in halogen ionization energy will reflect changes in this Madelung energy term. The more electropositive the metal, the higher charge it will carry and the more difficult it will be to ionize a neighbouring halogen electron. In contrast the cyclopentadienyl ligand is more polarizable and the charge it carries will readily respond to changes of electropositivity of the metal. The changes in charge on the ring will be the dominant factor in determining the ligand ionization energy as discussed above.

Experimental

The compounds $An(\eta\text{-}C_5H_5)_4$, $U(\eta\text{-}C_5H_5)_3 \cdot THF$ and $(M(\eta\text{-}C_5H_5)_2Cl)_2$ were prepared according to literature mehods [27—30]. The compounds $U(\eta\text{-}C_5H_5)_3Cl$, $Th(\eta\text{-}C_5H_5)_3Cl$ and $U(\eta\text{-}C_5Me_5)_2Cl_2$ were prepared by refluxing the appropriate cyclopentadienyltris-n-butyltin reagent with UCl_4 or $ThCl_4$.

The spectra were obtained using a Perkin-Elmer PS 16/18 photoelectron spectrometer fitted with a Helectros lamp capable of providing both He-I and He-II radiation. Xenon, nitrogen and the helium self-ionization band were used for spectral calibration.

Acknowledgements

We wish to thank Professor Lappert for helpful discussions, the S.R.C. for financial support and Charlie Eigenbrot for his peripatetic role.

References

1 J.P. Clark and J.C. Green, J. Organometal. Chem., 112 (1976) C14.
2 J.P. Clark and J.C. Green, J. Chem. Soc. Dalton, (1977) 505.
3 I.L. Fragala, G. Condorelli, P. Zanella and E. Tondello, J. Organometal. Chem., 122 (1976) 357.
4 I.L. Fragala, R.D. Fischer, C.R. Sienel, P. Zanella and E. Ciliberto, J. Organometal. Chem., 120 (1976) C9.
5 A.J. Downs, R.G. Egdell, A.F. Orchard and P.D.P. Thomas, J. Chem. Soc. Dalton, (1978) 1755.
6 Y. Baer and G. Busch, J. Electr. Spectros. Rel. Phen., 5 (1974) 611.
7 P.A. Cox, Structure and Bonding, 24 (1975) 59.
8 S. Evans, M.L.H. Green, B. Jewitt, A.F. Orchard and C.F. Pygall, J. Chem. Soc. Farad II., (1972) 1847.
9 S. Evans, M.L.H. Green, B. Jewitt, G.H. King and A.F. Orchard, J. Chem. Soc. Farad. II, (1974) 356.
10 C. Cauletti, J.C. Green, M.R. Kelly, P. Powell, J. van Tilborg, J. Robbins and J. Smart, J. Electr. Spectros. Rel. Phen., 19 (1980) 327.
11 A.F. Reid, D.E. Scaife and P.C. Wailes, Spectrochem. Acta, 20 (1964) 1257.
12 S. Evans, J.C. Green, S.E. Jackson and B. Higginson, J. Chem. Soc. Dalton, (1974) 304.
13 J.H. Burns, W.H. Baldwin and F.H. Fink, Inorg. Chem., 13 (1974) 1916.
14 P.G. Laubereau and J.H. Burns, Inorg. Nucl. Chem. Lett., 6 (1970) 59.
15 J. Muller, Chem. Ber., 102 (1969) 152.
16 J.L. Thomas and R.D. Hayes, J. Organometal. Chem., 23 (1970) 487.

17 R.G. Egdell, D. Phil. Thesis, Oxford, 1977.
18 S.A. Cotton, J. Organometal. Chem. Libr., 3 (1977) 189.
19 N. Beatham, P.A. Cox, A.F. Orchard and I.P. Grant, Chem. Phys. Lett., 63 (1979) 69.
20 D. Johnston, R. Satten and E. Wong, J. Chem. Phys., 44 (1966) 687.
21 J.L. Atwood and K.D. Smith, J. Chem. Soc. Dalton, (1973) 2487.
22 E.C. Baker, L.D. Brown and K.N. Raymond, Inorg. Chem., 14 (1975) 1376.
23 J. Müller, Chem. Ber., 102 (1969) 152.
24 R.G. Egdell, A.F. Orchard, D.R. Lloyd and N.V. Richardson, J. Electr. Spectros. Rel. Phen., 12 (1977) 415.
25 C. Cauletti, J.P. Clark, J.C. Green, S.E. Jackson, I.L. Fragala, E. Ciliberto and A.W. Coleman, J. Electr. Spectros. Rel. Phen., 18 (1980) 61.
26 J.M. Manriquez, P.J. Fagan and T.J. Marks, J. Amer. Chem. Soc., 100 (1978) 3939.
27 E.O. Fischer and Y. Hristidu, Z. Naturforschung, 176 (1962) 275.
28 E.O. Fischer and A. Treiber, Z. Naturforschung, 176 (1962) 276.
29 B. Kanellakopulos, E.O. Fischer, E. Dornberger and F. Baumgartner, J. Organometal. Chem., 24 (1970) 507.
30 R.E. Maginn, S. Manastyrskyj and Dubeck, J. Amer. Chem. Soc., 85 (1963) 672.