

Journal of Organometallic Chemistry, 326 (1987) 49-58
Elsevier Sequoia S.A., Lausanne - Printed in The Netherlands

PHOTOELECTRON SPECTROSCOPY OF *f*-ELEMENT ORGANOMETALLIC COMPLEXES

VII *. STUDIES OF DI-CYCLOPENTADIENYLURANIUM(IV) COMPLEXES CONTAINING TETRAHYDROBORATE, AMIDO, PIVALATE AND DITHIOCARBAMATE LIGANDS

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(Received October 27th, 1986)

Summary

A study of gas phase photoelectron spectra of a series of $U(\eta^5-C_5H_5)_2X_2$ ($X = BH_4, NEt_2, O_2CC(CH_3)_3, S_2CNEt_2$) complexes has revealed changes in the sequence of upper filled molecular orbitals along the series. In all cases the first ionization event corresponds to removal of uranium *5f* electrons. In the case of $X = NEt_2$, the next highest occupied ligand-based MO is an almost pure $N2p$ lone pair, but in the other complexes this MO is π -ring in nature. The observations are consistent with the higher reactivity of the amido complexes toward molecules containing polar double bonds or acidic hydrogens and with the greater labilities of the U-Cp bonds in the other complexes.

Introduction

Although MCp_2X_2 complexes (Cp = $\eta^5-C_5H_5$, X = halide, alkyl or aryl) are central to the organometallic chemistry of the early transition metals, the synthesis of the corresponding actinide derivatives remains elusive [1]. The logical point of entry into this area, UCp_2Cl_2 , was shown to be incorrectly formulated [2,3]; it

* For part VI see ref. 6f.

appears to undergo rapid ligand redistribution, mostly to UCp_3Cl and UCpCl_3L_2 ($\text{L} = \text{THF}$, $2\text{L} = \text{DME}$). The most successful method of stabilizing UCp_2X_2 species involves the use of the bulky permethylated anionic ligand $(\text{C}_5(\text{CH}_3)_5)^-$, hereafter denoted by Cp' [4]. Nevertheless normal UCp_2L_2 type compounds can be isolated [5] by employing the π donor NR_2 ligands or chelating ligands capable of saturating the coordination sphere of the uranium atom.

The electronic structures of $\text{U}(\text{Cp}')_2\text{X}_2$ and $\text{U}(\text{Cp})_2\text{X}_2$ ($\text{X} = \text{Cl}$, CH_3) complexes have recently been studied by gas-phase photoelectron (PE) spectroscopy and theoretical $\text{X}\alpha$ calculations [6a,7]. There have been no reports, however, on the electronic structure of other members of the UCp_2X_2 series even though they have an intriguing chemistry because, depending on the nature of the bonded X groups, the compounds have different chemical reactivities [1,5]. As part of our investigations of organometallic [6] and classical coordination compounds [8] of the actinide elements, we thus initiated a study of the electronic structure of $\text{U}(\text{Cp})_2\text{X}_2$ complexes, and in this paper we report on complexes in which $\text{X} = \text{BH}_4$, NEt_2 , $\text{O}_2\text{CC}(\text{CH}_3)_3$, or S_2CNEt_2 . The choice of these complexes was dictated by their thermal stability in the vapor phase and their different chemical reactivities.

Experimental

The complexes were prepared by published methods [5] and sent Catania sealed under argon. Before the recording of the PE spectra the purities of the compounds were checked by mass spectrometry. Only in the case of $\text{U}(\text{Cp})_2(\text{NEt}_2)_2$ was further purification necessary and this was carried out by dissolving complex in n-hexane and then reisolating it. All the complexes were handled under purified N_2 in a glove-box or in Schlenk glass. The spectra were recorded on a PS 18 Perkin-Elmer spectrometer modified by the inclusion of a hollow cathode discharge source giving a high output of HE-II photons (Helectros Development Corp.). The spectra were accumulated in the "multiple scan mode" with the aid of a Mostek Computer directly interfaced to the spectrometer. The energy scale of consecutive scans was locked to the argon $^2\text{P}_{3/2}$, $^2\text{P}_{1/2}$ lines and to the He $(1s)^{-1}$ self-ionization. Resolution of spectra of $\text{U}(\text{Cp})_2(\text{NEt}_2)_2$ was carried out by fitting the spectral profiles with asymmetrical Gaussian components after subtraction of the background. Particular care was necessary in recording the spectrum of $\text{U}(\text{Cp})_2(\text{NEt}_2)_2$, since sublimation (10^{-4} torr) of this complex at 120°C has been reported to produce mixtures of $\text{U}(\text{Cp})_2(\text{NEt}_2)_2$ and $\text{U}(\text{Cp})_3\text{NEt}_2$ [5a] and so we determined the spectrum at the lowest temperature permitting the recording of a sizable PE signal (80°C , 100 counts/s in the He-I). The spectrum did not change in the 80 – 100°C range, but at higher temperatures it was dominated by bands due to the free Cp ligand. To confirm the identity of species present in the vapor phase at that temperature we also ran the spectrum of $\text{U}(\text{Cp})_3\text{NEt}_2$, which was similar to that of $\text{U}(\text{Cp})_2(\text{NEt}_2)_2$, but as expected, the band assigned to ionization of the $\sigma(\text{U}-\text{N})$ bond was about one-half as intense as in $\text{U}(\text{Cp})_2(\text{NEt}_2)_2$. Except for $\text{U}(\text{Cp})_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_2$, which is a dimer, the complexes are monomeric in solution [5]. The mass spectra of all the compounds show strong molecular ion peaks. Only in the case of the bis(pivalate) complex were peaks above the molecular ion observed; it has been suggested that these may be due to recombination processes upon fragmentation [5c].

Discussion

The $U(Cp)_2X_2$ complexes all possess a pseudo-tetrahedral arrangement of the ligands around the uranium atoms with pentahapto bonded Cp rings [5,9]. Obviously, the site symmetries are different depending upon the denticity of X. The bis(amido) complex has pseudo-tetrahedral geometry [5a], while the bis(tetrahydroborate) complex has a higher coordination number because of the tridentate character of the BH_4 ligands [9]. The complexes containing the bidentate pivalate and dithiocarbamate ligands have pseudo-octahedral coordination geometries with *cis*-configurations [5b,c].

Spectroscopic PE data and theoretical $X\alpha$ results for some closely related compounds provide a basis for discussing the electronic structure of the $U(Cp)_2X_2$ complexes under consideration here. There is indication that, despite the lower symmetry, the molecular orbitals (MOs) responsible for the U-Cp bonding are not significantly admixed with those related to the U-X bonds. Of course, the energy ordering of upper filled MOs of each complex depends on the nature of the

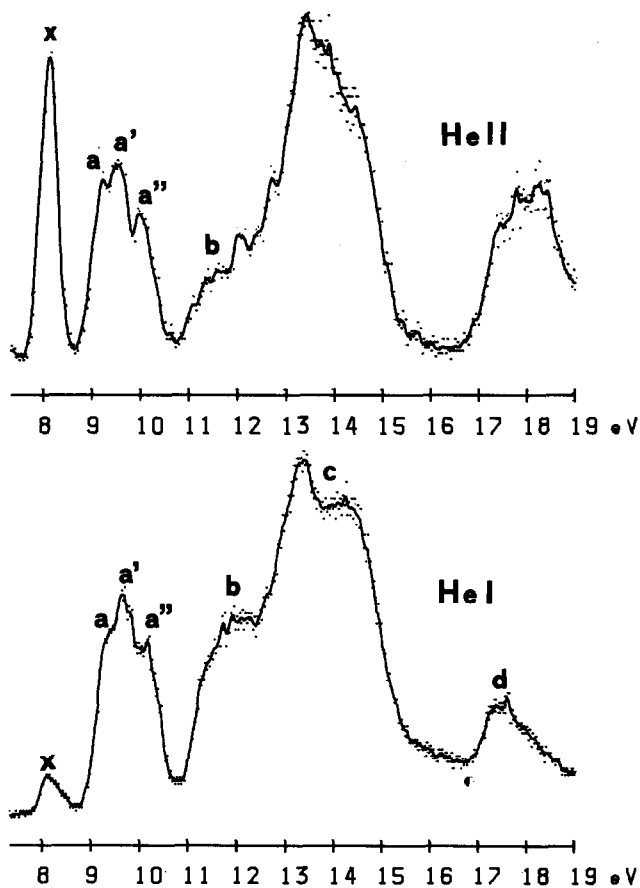


Fig. 1. He-I and He-II spectra of $U(\eta^5-C_5H_5)_2(BH_4)_2$.

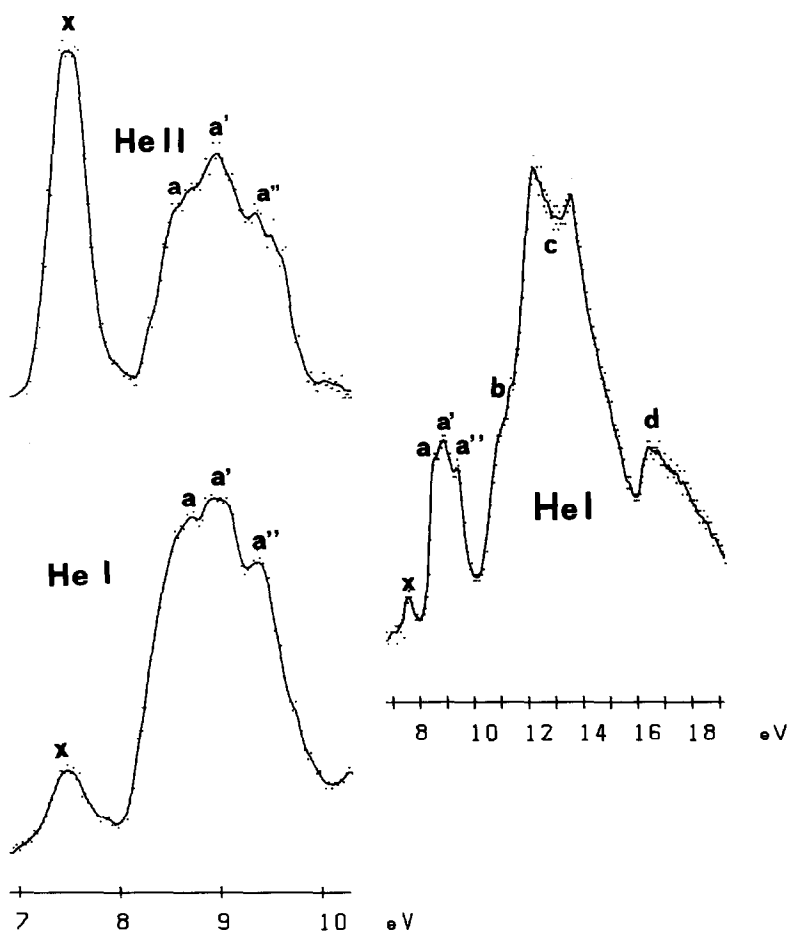


Fig. 2. He-I and He-II spectra of $U(\eta^5-C_5H_4CH_3)_2(BH_4)_2$. On the left: close-up of the lower IE regions. On the right: full scale He-I spectrum.

σ -bonded X group [6a,7]. The PE spectra of the complexes all show close similarities, the only exception being the spectrum of $U(Cp)_2(S_2NCeEt_2)_2$, which has a more complicated profile. The spectra consist (Fig. 1-5) of five groups of bands in the region up to 18 eV (*X*, *a*, *b*, *c*, and *d*). Comparison with PE and theoretical data for closely related complexes [6a,7] allows us to assign each of these bands to ionizations from sets of MOs which, within a localized bonding model, represent homogeneous groups of bonds. There is no doubt that the onset band *X* is due to the production of the $^2F_{5/2}$ final ion state upon removal of one electron from the 3H_4 , ground $U5f^2$ configuration [6]. The band envelope *a* certainly represents ionizations from MOs which are symmetry combinations of the e_1'' (in D_{5h} symmetry) MOs on each Cp ring.

In the case of $R = NEt_2$ (vide infra), the band must also include ionization from the $N2p$ lone pairs. The band *b* relates to the $\sigma(U-X)$ bonds and, finally, the bands *c* and *d*, common features in the spectra of all the Cp containing complexes, represent more internal ligand-based π and σ orbitals [6,10]. A more detailed

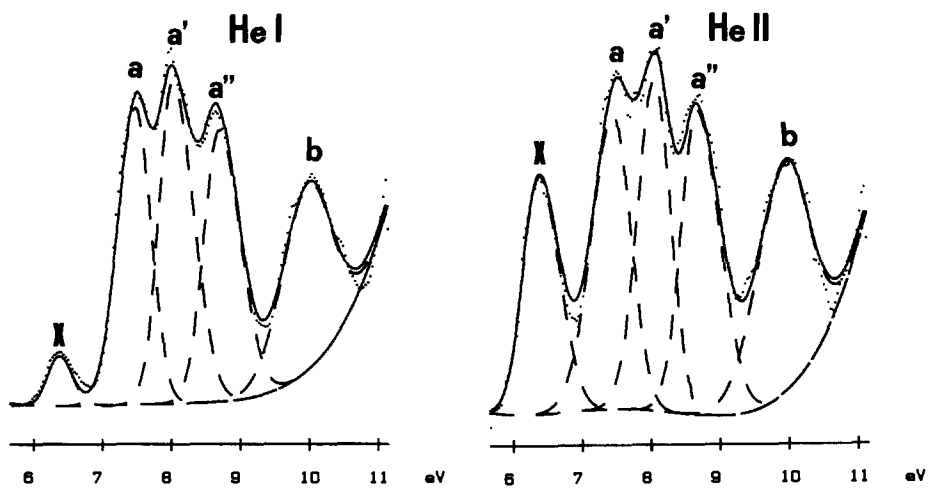


Fig. 3. He-I and He-II spectra of $U(\eta^5-C_5H_5)_2(NEt_2)_2$. Close-up of the lower *IE* regions.

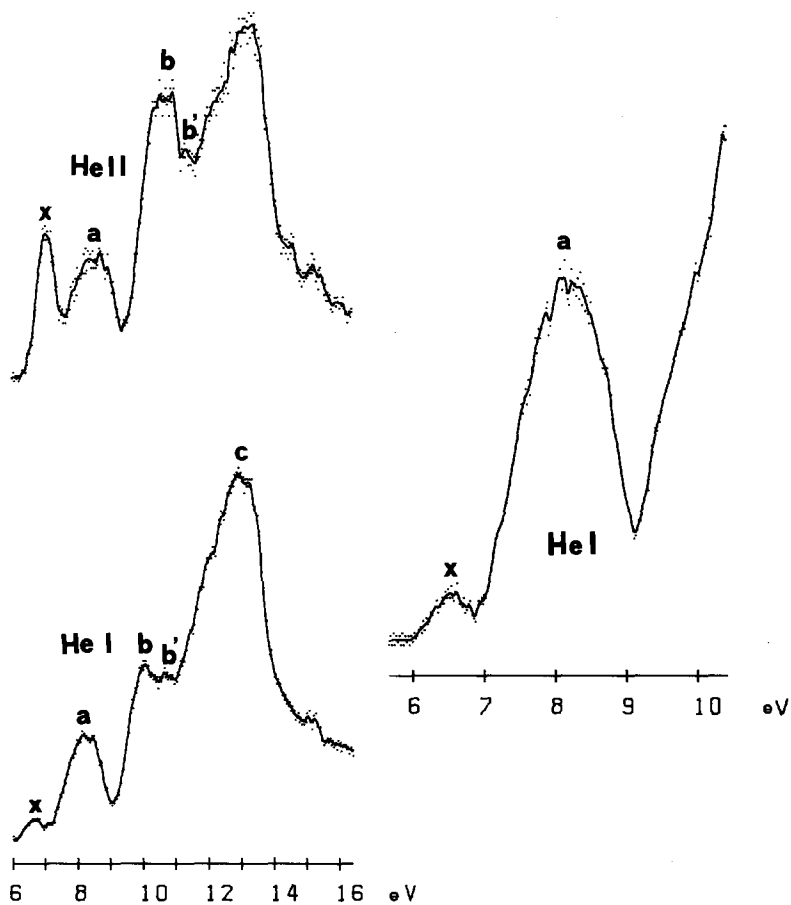


Fig. 4. He-I and He-II spectra of $U(\eta^5-C_5H_5)_2(O_2CC(CH_3)_3)_2$. On the left: full scale spectra. On the right: the He-I lower *IE* region.

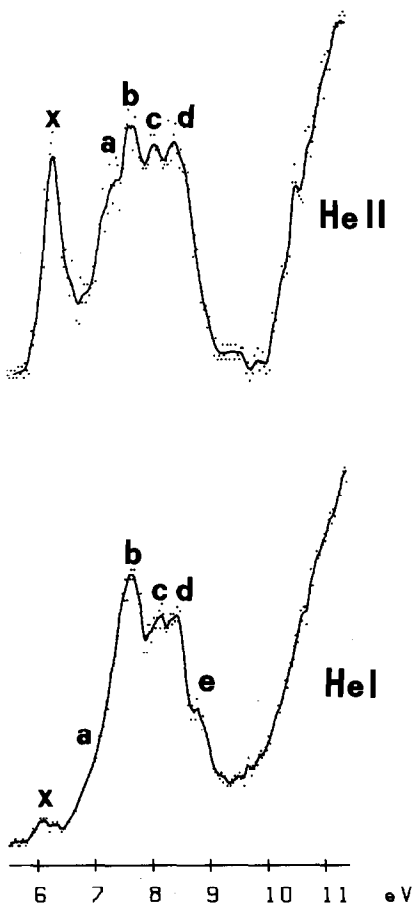


Fig. 5. He-I and He-II spectra of $U(\eta^5C_5H_5)_2(S_2CNEt_2)_2$. Close-up of the lower *IE* regions.

interpretation can be obtained by analysing the relevant PE data of each complex (Table 1).

The complexes $U(Cp)_2(BH_4)_2$ and $U(CpMe)_2(BH_4)_2$ show similar spectra (Fig. 1,2). Apart from the onset band *X*, which will be discussed later, the band envelope *a* can be seen to have three components having approximate relative intensity ratios 1/2/1. There is no doubt that they represent ionizations from MOs which are the symmetry combinations (a_1 , a_2 , b_1 , b_2 , in C_{2v} symmetry) of the four e_1'' (π_2 -Cp) MOs.

It is noteworthy that the grouping provided by the present intensity ratios agrees well with that inferred from $X\alpha$ calculations [7] for $U(Cp)_2Cl_2$ ($9b_2 > 13a_1 \approx 10b_1 > 6a_2$). The *IE* difference between the two extreme components is comparable to that observed in relevant $U(Cp')_2X_2$ complexes [6a], but, as expected, is smaller than those in $U(Cp)_3X$ [6b] or in $U(Cp)_4$ complexes [6f]. However, the *IE* dispersion of π_2 -Cp MOs in the present complexes appears too high for mediation only by coulombic interligand repulsion. There must be sizable interactions, and hence sizable admixture between π_2 -Cp MOs and uranium 6*d* and 5*f* orbitals. These

TABLE 1
RELEVANT PE DATA OF $U(\eta^5-C_5H_5)_2X_2$ COMPLEXES.

| X | Band label | IE | | Assignments | |
|--|------------|--------------------------|------|---|--|
| BH ₄ | X | 7.97 (7.46) ^a | | ² F _{5/2} | |
| | a | 9.27 (8.55) | | a ₂ + b ₁ + b ₂ + a ₁ (π ₂ (Cp)) | |
| | a' | 9.51 (8.80) | | | |
| | a'' | 9.98 (9.37) | | | |
| | b | 11.84 (11.19) | | σ(B-H) (terminal) | |
| Intensities | | | | | |
| He-I He-II | | | | | |
| NEt ₂ | X | 0.20 | 1.45 | 6.24 | ² F _{5/2} |
| | a | 1.76 | 2.05 | 7.49 | b ₂ + a ₁ (N2p lone pair) |
| | a' | 2.00 | 2.00 | 7.98 | a ₂ + b ₁ + π ₂ (Cp) |
| | a'' | 1.95 | 2.15 | 8.65 | |
| | b | 2.00 | 2.25 | 10.03 | σ(U-N) (b ₂ + a ₁) |
| O ₂ CC(CH ₃) ₂ | X | | | 6.73 | ² F _{5/2} |
| | a | | | 8.20 | π ₂ (Cp) |
| | b | | | 10.00 | O2p (C=O lone pair) |
| | b' | | | 10.55 | O2p (C=O lone pair) |
| | b'' | | | 12.19 | π ₀ (C=O), σ(C-C) methyl |
| S ₂ CNEt ₂ | X | | | 6.19 | ² F _{5/2} |
| | a | | | 7.24 | π ₂ (Cp) |
| | b | | | 7.79 | π ₃ + n ⁻ (thiocarbamate) |
| | c | | | 8.33 | π ₂ (Cp) |
| | d | | | 8.65 | π ₂ (thiocarbamate) |
| | e | | | 8.98 | n ⁺ (thiocarbamate) |

^a Values in parentheses refer to the $U(\eta^5-C_5H_4CH_3)_2BH_4)_2$ complex

conclusions, expected because of the lower symmetry of $U(Cp)_2X_2$ complexes, are well in line both with the trend of relative intensity changes of the components of the envelope *a* on passing to the He-II spectra and with the results of *Xa* calculations of $U(Cp)_2Cl_2$ [7]. Thus, no variations are observed in the relative intensities upon changing to the He-II ionizing source, indicating a similar make-up of these MOs in terms of U5*f* and of U6*d* subshell contributions.

The assignment of the next band *b* is quite straightforward. Reference to PE data for various BH₄-containing complexes [11] suggests that the band must represent ionizations of terminal σ(B-H) bonds. The trend of the He-I vs. He-II relative intensity variation of band *b* reinforces this conclusion. The band decreases (relative to *a*) in the He-II spectra, as expected in view of the smaller H1s/C2*p* cross-section ratio under the more energetic He-II radiation [11].

In the spectrum of $U(Cp)_2(NEt_2)_2$, the band envelope *a* is resolved into three components (Fig. 3) of almost similar relative intensities (Table 1). The overall *IE* separation is somewhat greater (ΔIE 1.19 eV) than in the case of the BH₄ complexes (Table 1) because of the presence in the same spectral region of two new ionizations (in addition to those of π₂-Cp MOs) necessarily absent from the spectra of BH₄ complexes, from MOs which represent the symmetry combinations of N2*p* lone pairs. Reference to published data on several transition metal amido complexes indicates that these ionizations are always in the 6.5–8 eV region [12], and that their

total energy dispersions, necessarily dependent upon the various molecular symmetries, range from 0.92–0.75 eV in $M(\text{NEt}_2)_4$ ($M = \text{Ti, Zr, Hf}$) [12a] to 0.44–0.86 eV in $M(\text{N}(\text{SiMe}_3)_2)_3$ ($M = \text{Sc, Ti, Cr, Fe}$) [12b] and to 1.28–0.83 eV in $M(\text{N}(\text{SiMe}_3)_2)_2$ ($M = \text{Ge, Sn, Pb}$) [12c] while in $M(\text{N}(\text{SiMe}_3)_2)_3$ ($M = \text{Ga, In}$) these ionizations appear as a single band around 8.39 eV [12b]. In the present case there is little doubt that the first component a represents the local out-of-phase combination of $\text{N}2p$ lone pairs (b_2 in C_{2v} symmetry). The ionization of the in-phase combination a_1 might contribute to the envelope $a'-a''$ or, alternatively, it might have an energy near to that of the b_2 combination, thus giving the band a alone; we favour the latter alternative, because (i) the He-I relative intensity of band a indicates (Table 1) that it must represent two ionization events and (ii) it is unlikely that it is one of the $\pi_2\text{-Cp}$ ionizations which contributes to the total intensity of this band. If there were such a contribution the total energy dispersion of $\pi_2\text{-Cp}$ based MOs would be greater than that generally observed (Table 1) in $\text{U}(\text{Cp})_2\text{X}_2$ complexes [6a]. Finally, the moderate, though definite, increase in the intensity of band a (relative to the remaining envelope $a'-a''$) in the He-II spectrum (Table 1) reflects the usual behavior of the $\text{N}2p/\text{C}2p$ cross-section ratio on changing from He-I to He-II excitation [13]. Therefore, given that band a refers to the ionizations from $\text{N}2p$ lone pair combinations, the remaining bands a' and a'' must necessarily refer to the ionizations of $\pi_2\text{-Cp}$ MOs. Their IE separation is now entirely in accordance with the value for the BH_4 complex. The next band b lies in the region where ionization from $\sigma(\text{M}-\text{N})$ bonds is expected. In contrast to the results for almost all the amido complexes reported to date [12], the band is well resolved, and has a half-width of ≈ 1 eV. In the C_{2v} point group, $\sigma(\text{U}-\text{N})$ bonds give rise to two combinations of b_2 and a_1 symmetry. It is unlikely that the band b relates only to the upper-lying b_2 combination. The half-width appears to be too large [14], while the He-I intensity of the band relative to the total intensity [15] of the envelope a ($5.7/2$) is near to that expected for any occupancy ratio $6/2$ [$(a_2 + b_1 + a_1 + b_2 (\pi_2\text{-Cp})) + (a_1 + b_2 (\text{N}2p)) / (a_1 + b_2 (\sigma(\text{U}-\text{N})))$]. It is noteworthy that this band shows a slight increase in the He-II spectrum, indicating a possible metal contribution to the corresponding MOs.

The pivalate complex $\text{U}(\text{Cp})_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_2$ possesses a pseudooctahedral geometry with a *cis*-configuration of the ligands. In view of the more sterically crowded coordination environment it is expected that inter-ligand repulsion will play a more dominant role in determining the IE s of the various MOs. Indeed band a now appears a featureless structure having a half-width of ≈ 1.3 eV (Fig. 4); we believe that this is due to a stronger repulsion within the $(\text{Cp})_2$ framework, which results in severe overlap of the bands due to $\pi_2\text{-Cp}$ combinations. Next, the band b is resolved into two components (b, b') having an IE separation of 0.55 eV reference to PE data for several carboxylic acids and of their esters [16] suggests that the bands represent symmetry combinations of MOs mainly localized on carbonyl $\text{O}2p$ lone pairs. It has been noted that the band c , which follows, represents ionization of more internal π and σ MOs mostly localized on Cp rings, but in the present case the low IE tail of the band appears more structured than in previous cases. The new features represent ionizations either from $\sigma(\text{C}-\text{C})$ (methyl) bonds of pivalate ligands or from carbonyl $\pi(\text{C}=\text{O})$ bonds [16].

Finally we discuss the spectrum of $\text{U}(\text{Cp}_2)(\text{S}_2\text{CNET}_2)_2$ (Fig. 5). In this case the spectral region between 7 and 10 eV appears to be much more complicated than is

the case for spectra of the complexes previously discussed. Five bands, labelled *a*, *b*, *c*, *d*, and *e* in the Fig. 5, can be identified. It has been reported [17] that the 7–10 eV region in the PE spectra of various dithiocarbamate complexes of transition metal ions is dominated by ionization from MOs, mainly $S3p$ in character, localized on the $\overline{SMSCNet}_2$ system. There are two π (π_2 and π_3) and two σ (M–S) ($n+$ and $n-$) MOs. The energy ordering of these MOs ($\pi_3 > n- > \pi_2 > n+$) as well as their energy separation seem not to be strongly dependent on the geometries around the central metal atom [17]. It follows that some of the bands *a–e* must be assigned to such ionizations. The feature *e* at 8.98 eV certainly belongs to the ionization of one $S3p$ based MO, since the band is no longer discernible in the higher *IE* tail of the band envelope *a–e* in the He-II spectrum. This behaviour parallels the dramatic fall-off (relative to $C2p$) of $S3p$ cross-section under He-II radiation [13]. Consideration of *IE*s reported for relevant valence ionization in dithiocarbamate complexes [17] leads one to conclude that the band *e* must be assigned to the $n+$ MO. If it is assumed that the reported *IE*s separation among π_3 , $n-$, π_2 and $n+$ MOs is maintained in $U(Cp)_2(S_2CNet_2)$, it appears that the ionization from the remaining MOs must be represented by the bands *b* (π_3 and $n-$) and *d* (π_2). This assignment agrees well with the relative intensity decrease of band *b* on changing from the He-I to the He-II radiation. The He-II intensity variations of the bands *c* and *d* are uncertain because they are strongly overlapped. This assignment then, leaves bands *a* and *c* for $\pi_2(Cp)$ ionizations.

Finally we discuss the onset band *X*, a common feature of all the spectra under consideration. The very large increase in the band intensity in the He-II spectra is unequivocal confirmation for the assignment of this band to ionization of $U5f^2$ electrons [6,8]. The pattern of final state structure expected on ionizing one $5f^2$ electron from 3H_4 ground configuration of $5f^2$ uranium compounds has been discussed previously [6,11]. There is no doubt that of the two $^2F_{5/2}$ and $^2F_{7/2}$ final states which can be reached upon ionization from the ground $5f^2$ configuration, only the $^2F_{5/2}$ can result in observable PE bands. The PE intensity ratio of the two final state peaks, although dependent on the mechanism of ground state coupling (Russel–Saunders or *j-j*), is in both cases extremely unfavorable for detection of the $j 7/2$ state. Moreover, the energy separation ($7/2\xi 5f$) between the two $j 5/2$ and $7/2$ states, obviously not dependent on the coupling scheme, would, in the present case, preclude the observation of the $j 7/2$ state because the PE $^2F_{5/2}$ peak lies close to the more intense band envelope, which would hide any low intensity structure.

Conclusion

This study provides evidence for marked variations in the electronic structure of the $U(Cp)_2X_2$ complexes considered. The variations depend on the nature of the X ligands and may be responsible for the different chemical reactivities. In the case of $X = BH_4$, the highest ligand-based MO is one of the four π_2-Cp symmetry combinations, and the corresponding *IE* value is the highest observed for the $U(Cp)_2X_2$ and $U(Cp')_2X_2$ complexes so far studied [6a]. This observation is consistent with the high stability, and, hence, the low reactivity of the complex. The amido complex displays a different behaviour. In this case the ligand-based HOMO is almost pure $N2p$ lone pair in character; this is consistent with the higher reactivity of the

complex toward molecules containing dipolar double bonds and acidic hydrogens [5].

Finally, in the pseudo-octahedral pivalate and dithiocarbamate complexes the ligand-based HOMO is Cp in character but lies very close to MOs centered on the X ligands. This small energy difference, however, appears to render the U–Cp bond more vulnerable. whereas for the amido complex, mass spectroscopic data indicate that the $\sigma(\text{U–N})$ bond is easily broken, in these complexes the U–Cp bonds are the more labile [5]. Of course the greater the strength of U–S or U–O than of U–N bonds may also be responsible for this observation, and must not be forgotten when discussing the overall labilities and stabilities of the complexes.

Acknowledgements

The authors thank Prof. T.J. Marks (Northwestern University) for helpful discussions and the Consiglio Nazionale delle Ricerche (C.N.R., Rome) for financial support. One of us (I.F.) also thanks NATO for a travel grant (068/84).

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