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# He(I) photoelectron spectroscopic study of half- and bent sandwich tetrahydroborates

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**Abstract**

The He(I) ultraviolet photoelectron spectra of $CpZr(BH_4)_3$, $Cp_2Zr(BH_4)_2$, $Cp_2Hf(BH_4)_2$, $Cp_2Ta(BH_4)$ and $Cp_2TaH_3$ are reported. A tentative assignment is given for the low energy part of the spectra. At higher energies, cyclopentadienide ionizations merge with the borohydride ionizations resulting in a complicated overlapped band structure. As a consequence no photoelectron spectroscopic evidence can be given concerning the ligation of the tetrahydroborate groups.

*Keywords:* Zirconium; Hafnium; Tantalum; Boron; Photoelectron spectroscopy

## 1. Introduction

Transition metal tetrahydroborates have aroused much attention from both structural and practical points of view. Structural studies were frequently centred on the ligation of the tetrahydroborate group(s) to the central metal atom; tridentate, bidentate and monodentate cases are known from the literature [1]. From the practical point of view, transition metal tetrahydroborates (containing only metal and tetrahydroborate groups) are ideal precursors for the chemical vapour deposition (CVD) of boride thin films [2]. Furthermore, cyclopentadienyl zirconium and hafnium tetrahydroborates were successfully used as precursors to metal carbide [3] and carbide–boride [4] hard coatings by CVD.

As far as electronic structure is concerned, tetrahydroborates of Ti [5], Zr, Hf [6,7], Al and U [7] have been thoroughly studied by UV photoelectron spectroscopy (UPS). Less attention has been devoted to the mixed cyclopentadienyl tetrahydroborates. To the best of our knowledge, their photoelectron spectra have not yet been published. Only the electron diffraction and an EHMO study of $(\eta^5-C_5H_5)Zr(BH_4)_3$ could be found in the literature [8].

However, bent biscyclopentadienyl metal complexes containing ligands other than tetrahydroborate have been extensively investigated by UPS [9,10] and bonding schemes for these molecules have been analysed in detail [11].

We report here the He(I) photoelectron spectra of some half- and bent ($\eta^5$-cyclopentadienyl) tetrahydroborates of Zr, Hf and Ta which are tentatively assigned with the help of calculations presented in Ref. [8] and comparisons with the spectra of related molecules.

## 2. Experimental

$\eta^5$-Cyclopentadienyl (Cp) tetrahydroborates $CpZr(BH_4)_3$ (**I**), $Cp_2Zr(BH_4)_2$ (**II**), $Cp_2Hf(BH_4)_2$ (**III**) and $Cp_2Ta(BH_4)$ (**IV**) were prepared by standard literature methods based on the reaction between corresponding metal cyclopentadienyl halides and lithium (or sodium) tetrahydroborate [8,12–14]. As a result of an unsuccessful attempt to synthesize **IV**, $Cp_2TaH_3$ (**V**) was formed and also studied. Purity was checked by elemental analysis and mass spectrometry.

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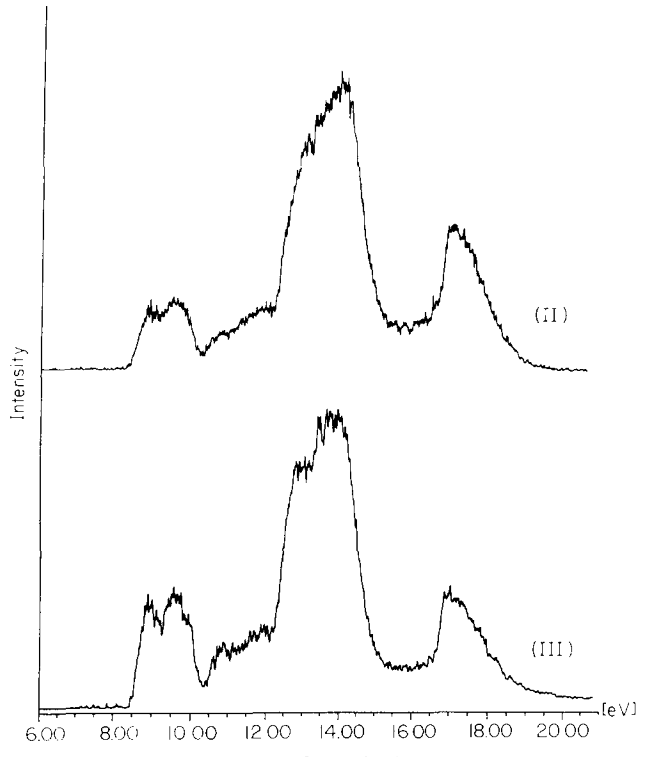

Fig. 1. He(I) photoelectron spectra of $(\eta^5\text{-}C_5H_5)_2Zr(BH_4)_2$ (**II**) and $(\eta^5\text{-}C_5H_5)_2Hf(BH_4)_2$ (**III**).

The photoelectron spectra were recorded on a Leybold-Heraeus UPG 200 spectrometer (**II**, **III**), and on an Atomki ESA 32 instrument (**I**, **IV**, **V**) by using a heated direct inlet probe. The spectra were calibrated using argon as an internal standard. Maximum errors in ionization energies are estimated to be 0.1 eV.

## 3. Results

The He(I) photoelectron (PE) spectra are shown in Figs. 1 and 2. Ionization energies (*IE*) together with those of related compounds are given in Table 1.

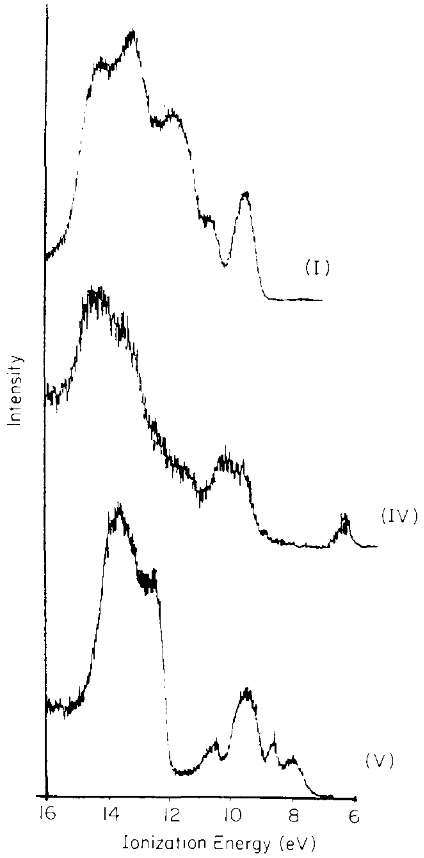

Fig. 2. He(I) photoelectron spectra of $(\eta^5\text{-}C_5H_5)Zr(BH_4)_3$ (**I**), $(\eta^5\text{-}C_5H_5)_2Ta(BH_4)$ (**IV**) and $(\eta^5\text{-}C_5H_5)_2TaH_3$ (**V**).

## 4. Discussion

All the investigated molecules with the exception of $CpZr(BH_4)_3$ contain bent $Cp_2M$ and $BH_4^-$ fragments, both of which have been discussed in detail in the literature. In two subsequent papers, Green and coworkers [9,10] published the PE spectra of various biscyclopentadienyl metal derivatives. The spectra are clearly interpreted on the basis of a molecular orbital scheme which has been derived by the interaction of

Table 1
Vertical ionization energies (eV) of the investigated cyclopentadienyl derivatives and related molecules

| $CpZr(BH_4)_3$ | $Cp_2Zr(BH_4)_2$ | $Cp_2ZrCl_2$ $^{a}$ | $Cp_2Hf(BH_4)_2$ | $Cp_2HfCl_2$ $^{a}$ | $Cp_2Ta(BH_4)$ | $Cp_2TaH_3$ |
|---|---|---|---|---|---|---|
| 9.5 | 8.9 | 8.6 | 8.9 | 8.9 | 6.3 | 8.0 |
| 10.7 $^{b}$ | 9.5 | 9.1 | 9.5 | 9.3 | 9.5 | 8.7 |
| 11.9 | 9.8 $^{b}$ | 9.8 | 9.9 | 10.0 | 10.2 | 9.5 |
| 13.2 | | 10.5 | | 10.6 | 12.6 $^{b}$ | 10.5 |
| 14.2 | | 11.1 | | 11.3 | 13.7 | 12.7 |
| | | 11.3 | | 11.6 | 14.3 | 13.7 |
| | 13.0 | 13.1 | 13.0 | 13.2 | | |
| | 13.7 $^{b}$ | 13.8 | 13.4 $^{b}$ | 13.7 | | |
| | 14.1 | | 13.8 | | | |
| | 17.0 | 17.1 | 17.0 | 17.8 | | |
| | | 21.2 | | 21.5 | | |

[a] Ref. [10]; [b] shoulder.

the $Cp_2M$ fragment of $C_{2v}$ symmetry with corresponding ligand orbitals. In their broad-scale study Lauher and Hoffmann [11] formulated a model for the electronic structure of $Cp_2ML_n$-type molecules showing that the three lowest $Cp_2M$ frontier orbitals, $1a_1$, $b_2$ and $2a_1$, play a prime role in coordinating further ligands.

In agreement with experimental findings, in **I** tridentate [8] and in **II–IV** bidentate modes of coordination of the $BH_4^-$ ligands can be suggested [1]. As shown, in the tridentate mode of coordination the four occupied frontier orbitals of the ligand transform as $2 \times a_1 + e$ in $C_{3v}$ and in the bidentate case as $2 \times a_1 + b_1 + b_2$ in $C_{2v}$ local symmetry about the boron. In the latter case $2a_1$ and $1b_2$ orbitals are effective in electron donation to the metal [5].

### 4.1. Interpretation of spectra

#### $CpZr(BH_4)_3$

The He(I) PE spectrum of **I**, shown in Fig. 2, contains a well separated peak at 9.5 eV followed by a broad overlapped band with a shoulder at 10.7 eV and three distinct maxima at 11.9, 13.2 and 14.2 eV. There is little doubt that the first ionization energy can be attributed to the doubly degenerate $\pi$ set of the cyclopentadienide ligand. The broad envelope ranging from ca. 10 to 15 eV indicates that the higher cyclopentadienide ionizations merge with the borohydride ionizations. The EHMO energy-level diagram of Ref. [8] can be invoked for further assignment where the next molecular orbital of $a_2$ symmetry is localized on the $BH_4^-$ ligands. On the basis of energy and relative intensity, this orbital can be related to the shoulder at 10.7 eV. It is important to note that the difference in the calculated and observed ionization energies agrees well in the case of $IE_1$ and $IE_2$; the corresponding differences are 2.8 and 2.9 eV, respectively. The closely spaced set of orbitals below the first two energy levels has predominantly borohydride donor character, which is hard to relate to the three distinct maxima of the second PE band. In conclusion, the general feature of the PE spectrum is qualitatively reflected by the EHMO energy-level diagram of $CpZr(BH_4)_3$ considering triply bonded borohydride ligands around Zr.

#### $Cp_2Zr(BH_4)_2$ and $Cp_2Hf(BH_4)_2$

The PE spectra of **II** and **III** are very similar and can be discussed in relation to the photoelectron spectroscopy of $Cp_2ZrCl_2$ and $Cp_2HfCl_2$ [10]. We suggest bidentate metal–boron hydrogen bridges and $C_{2v}$ symmetry. The four donor orbitals of the two $BH_4^-$ ligands form $2 \times a_1$ and $2 \times b_2$ combinations, one of them having no proper symmetry to interact with the frontier orbitals of the $Cp_2Zr$ fragment.

The partly split band in the low ionization energy region of the spectra (8.9–10.0 eV) can be assigned to the metal–cyclopentadienide orbitals. In both cases only two vertical ionization energies and a shoulder can be distinguished. The ionization energy values are very similar to those of the corresponding chloro derivatives (see Table 1).

The next complex band in the region 13.0–14.0 eV is assigned to ionizations from borohydride and lower lying Cp orbitals of C–H and C–C bonds. As a consequence of the intensive overlapping, no further distinction can be made on this level of interpretation. Considering the grouping principle of biscyclopentadienyl metal dihalides in Ref. [10], the bistetrahydroborato derivatives belong to class A where the cyclopentadienide $e_1$ orbitals lie above the orbitals localized on the other ligands.

#### $Cp_2Ta(BH_4)$

To the best of our knowledge, the molecular structure of **IV** has not yet been determined, although similar compounds of Ti, $Cp_2Ti(BH_4)$ [15,16], and Nb, $Cp_2Nb(BH_4)$ [17], have been investigated. The experimental results make it likely that there are two bridging hydrogen atoms coordinated to the central metal atom. The same structure can be adopted also for $Cp_2Ta(BH_4)$.

In this case we have a $d^2$ compound and the first band at 6.3 eV can be associated with ionizations from orbitals of predominantly d character. This value agrees well with the first ionization energy of $Cp_2TaCl_2$ occuring at 6.4 eV and assigned to the removal of the odd d electron [10]. The band under discussion is not resolved and only its broadening reflects in certain sense to the ionization of singly occupied orbitals. The subsequent band, having two local maxima at 9.6 and 10.2 eV, is related to $C_5H_5$ ($\pi$) ionization, while higher ionizations between 11 and 15 eV result in a complex, overlapped band structure similar to the second band in the PE spectra of **II** and **III**.

The PE spectrum of $Cp_2TaH_3$ is essentially identical with that of Green et al. [9]. It is evident from the spectrum that higher Cp ionizations occur in the same energy range (12–15 eV) as those of the $BH_4^-$ group, making it difficult to identify them.

In summary, the He(I) photoelectron spectra of the investigated cyclopentadienyl tetrahydroborates provide only limited information concerning their electronic structure. In the case of $d^0$ complexes (**I–III**), $C_5H_5$ ($\pi$) ionization has the lowest energy demand resulting in the first band in the spectrum. The higher Cp and $BH_4^-$ ionizations coalesce into the second overlapped band. The $d^2$ complex (**IV**) has the same spectral features with an additional band at low energy assigned to the removal of d electrons.

The complex nature of the band centred at about 14 eV does not allow any kind of conclusion concerning the ligation of the tetrahydroborato group(s). This is not similar to the case of pure tetrahydroborates where PE spectroscopy is helpful in the diagnosis of the mode of ligation: $M(BH_4)_4$ vs. $Al(BH_4)_3$ [7]. Reliable quantum chemical calculations would be of great help in revealing further details of the spectra.

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