Our calculation supports alternative b. The difference between the Zr and the Hf complexes is a relativistic effect. The Hf 6s orbital lies lower than the Zr 5s orbital due to the relativistically increased effective mass of the electron.[34] Consequently, the Hf 6s orbital will mix stronger into the occupied a_1 orbitals of the borohydride complex. This is most noticeable for the $1a_1$ orbital where the metal population increases from 0.11 for M = Zr to 0.15 for M = Hf and leads to an enlarged covalent energy lowering. The effect in the $2a_1$ orbitals is smaller, but the corresponding shift of 0.38 eV is still larger than average. The total s population of Hf and Zr also reflect this difference (see Table V).

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Registry No. $Zr(BH_4)_4$, 12370-59-1; $Hf(BH_4)_4$, 37274-93-4; $Th(BH_4)_4$, 12523-76-1; $U(BH_4)_4$, 102630-71-7.

Contribution from the Inorganic Chemistry Laboratory, Oxford OX1 3QR, England,
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Photoelectron Spectra of Metal Tetrakis(methyltrihydroborates) and Thorium Tetrakis(tetrahydroborate)

Jennifer C. Green,[*,†] Ron Shinomoto,[‡] and Norman Edelstein[*,‡]

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He I and He II photoelectron spectra of $M(BH_3CH_3)_4$ (M = Zr, Hf, Th, U) and that of $Th(BH_4)_4$ in the vapor phase have been obtained. Assignments of the bands based on the $X\alpha$–SW calculations of Hohl and Rösch for $M(BH_4)_4$ are given.

Introduction

The volatile metal tetrahydroborates ($M(BH_4)_4$; M = Zr, Hf, Th, Pa, U, Np, Pu) have been the subject of structural, vibrational, optical, photoelectron (PE), and theoretical studies.[1-8] For the actinide tetrahydroborates, one of the major questions has been the extent of the f orbitals' involvement in the bonding in these complexes.[5,6] Unfortunately, the first three members of the actinide borohydride series, $Th(BH_4)_4$, $Pa(BH_4)_4$, and $U(BH_4)_4$, are polymeric in the solid state with a metal site symmetry much lower than the T_d symmetry found in the vapor phase.[9] Recently, the volatile compounds $M(BH_3CH_3)_4$ where M = Zr, Th, U, and Np have been synthesized and structurally characterized.[10] These studies have shown the metal ion is at a site of approximately T_d symmetry in the solid state. Magnetic measurements for both $U(BH_3CH_3)_4$ and $Np(BH_3CH_3)_4$ have been interpreted on this basis.[11-13]

Photoelectron spectra of $Zr(BH_4)_4$, $Hf(BH_4)_4$, and $U(BH_4)_4$ have been published and discussed previously by two groups.[5,6] Quasi-relativistic $X\alpha$-SW calculations of $M(BH_4)_4$ (M = Zr, Hf, Th, U) have been described and reproduced the ionization energies satisfactorily except for a uniform shift.[8] We report in this paper the photoelectron spectra of $M(BH_3CH_3)_4$ (M = Zr, Hf, Th, U) and, for completeness, $Th(BH_4)_4$. These spectra are assigned on the basis of their similarities to the $M(BH_4)_4$ compounds and the results of the $X\alpha$-SW calculations.

Experimental Section

Photoelectron spectra were obtained on a PES Laboratories 0078 spectrometer, with data collection either on an XY recorder or by means of a RML 380Z microprocessor. The spectra were calibrated by reference to Xe, N_2, and He. The methyltrihydroborate samples were prepared as described previously.[10] $Th(BH_4)_4$ was prepared as described by Katz and Hoekstra.[14]

Results

He I and He II spectra were obtained for $Th(BH_4)_4$ and $M(BH_3CH_3)_4$ (M = Zr, Hf, Th, U) in the vapor phase. Ionization energy (IE) data are given in Table I and representative spectra shown in Figures 1–5. The individual points give the raw data, whereas the solid line is a least-squares fit to these points.[15] As most of the bands were broad and featureless, they are not well characterized by the chosen IE, and identification of trends necessitates comparison of the whole band shape and position.

The PE spectra of the thorium and uranium tetrakis(methyltrihydroborates) show two bands (A and B) in the region 10–16 eV. $U(BH_3CH_3)_4$ has an additional band (f) at 8.3 eV, which shows a substantial intensity increase in the He II spectrum, and may be associated with ionization of the $5f^2$ electrons. Three further high-IE bands (C, D, E) are clearly defined in the He II spectrum of $Th(BH_3CH_3)_4$ (see Figure 3).

In contrast, the Zr and Hf analogues have an additional low-energy band (A′) with a maximum at circa 10.7 eV. Intensity comparisons suggest that this ionization comprises part of the first band A in the spectra of the actinide tetrakis(methyltrihydroborates). Otherwise, the spectra are very similar to those of their heavier congeners. There is a very low intensity band (f) at 24.7 eV visible in the He II spectrum of $Hf(BH_3CH_3)_4$. A similar band was found at 26.1 eV for $Hf(BH_4)_4$[5] and assigned to ionization of the 4f shell. The kinetic energy of band f, 16.1 eV, is very close to that of the He self-ionization band, 16.2 eV. In all the spectra measured here the latter tended to be suppressed at the pressure used for data collection and could only be observed at low com-

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[*] To whom correspondence should be addressed.

[†] Inorganic Chemistry Laboratory.

[‡] University of California.

(1) For a review of work prior to 1977 see: Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

(2) Bernstein, E. R.; Keiderling, T. A. *J. Chem. Phys.* **1973**, *59*, 2105.

(3) Banks, R. H.; Edelstein, N. M.; Spencer, B.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1980**, *102*, 620.

(4) Banks, R. H.; Edelstein, N. M. *J. Chem. Phys.* **1980**, *73*, 3589.

(5) Downs, A. J.; Egdell, R. G.; Orchard, A. F.; Thomas, P. D. P. *J. Chem. Soc., Dalton Trans.* **1978**, 1755.

(6) Hitchcock, A. P.; Hao, N.; Werstiuk, N. H.; McGlinchey, M. J.; Ziegler, T. *Inorg. Chem.* **1982**, *21*, 793.

(7) Mancini, M.; Bougeard, P.; Burns, R. C.; Mlekuz, M.; Sayer, B. G.; Thompson, J. I. A.; McGlinchey, M. J. *Inorg. Chem.* **1984**, *23*, 1072.

(8) Hohl, D.; Rösch, N. *Inorg. Chem.*, preceding paper in this issue.

(9) Bernstein, E. R.; Hamilton, W. C.; Keiderling, T. A.; LaPlaca, S. J.; Lippard, S. J.; Mayerle, J. J. *Inorg. Chem.* **1972**, *11*, 3009.

(10) Shinomoto, R.; Gamp, E.; Edelstein, N. M.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1983**, *22*, 2351.

(11) Rajnak, K.; Gamp, E.; Shinomoto, R.; Edelstein, N. M. *J. Chem. Phys.* **1984**, *80*, 5942.

(12) Rajnak, K.; Banks, R. H.; Gamp, E.; Edelstein, N. *J. Chem. Phys.* **1984**, *80*, 5951.

(13) Gamp, E.; Edelstein, N. *J. Chem. Phys.* **1984**, *80*, 5963.

(14) Hoekstra, H. R.; Katz, J. J. *J. Am. Chem. Soc.* **1949**, *71*, 2488.

(15) The smoothing method used fits a weighted polynomial to a number of points successively across the data set. The polynomial is weighted so that the fit is equivalent to a least-squares fit over each group of points. See: Savitzky, A.; Golay, M. J. E. *Anal. Chem.* **1964**, *36*, 1627.

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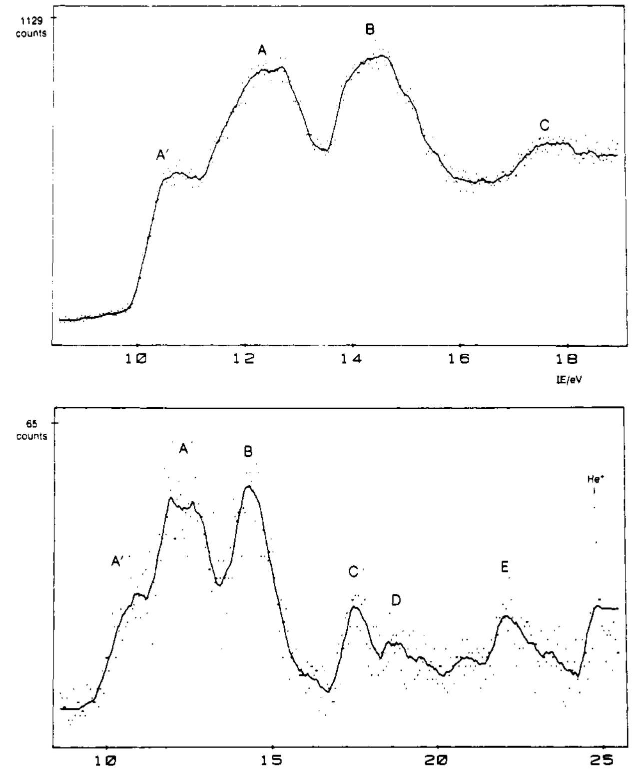

Figure 1. PE spectrum of $Zr(BH_3CH_3)_4$: upper, He I excitation; lower, He II excitation.

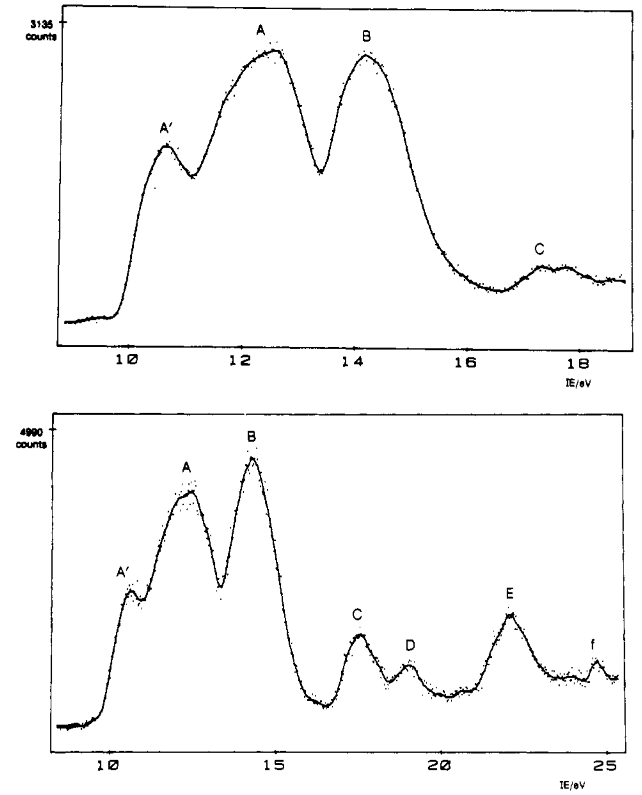

Figure 2. PE spectrum of $Hf(BH_3CH_3)_4$: upper, He I excitation; lower, He II excitation.

pound pressure. However, the relative intensities of band f and band E of $Hf(BH_3CH_3)_4$ were reproducibly the same whatever the experimental conditions. Also, the clear correspondence in intensity and position with the band reported for $Hf(BH_4)_4$[5] leads us to be confident of its assignment to a 4f ionization. A shift of 1.1 eV has been reported for the $4f^{7/2}$ binding energy between $U(BH_4)_4$ and $U(BH_3CH_3)_4$.[16]

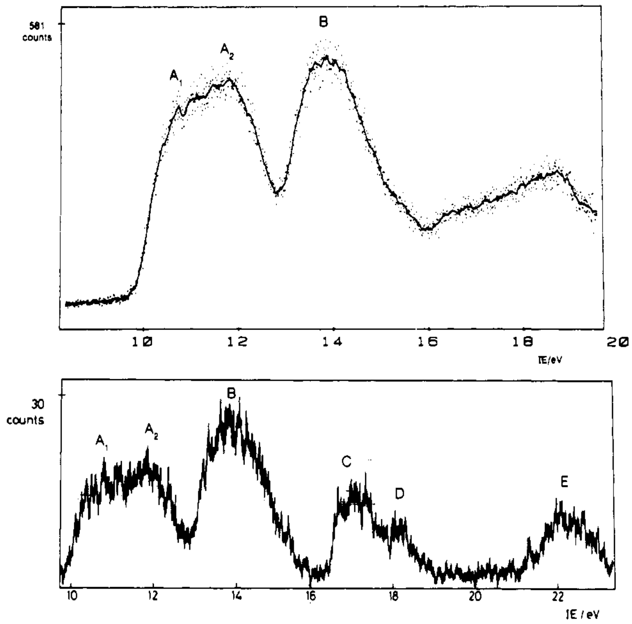

Figure 3. PE spectrum of $Th(BH_3CH_3)_4$: upper, He I excitation; lower, He II excitation.

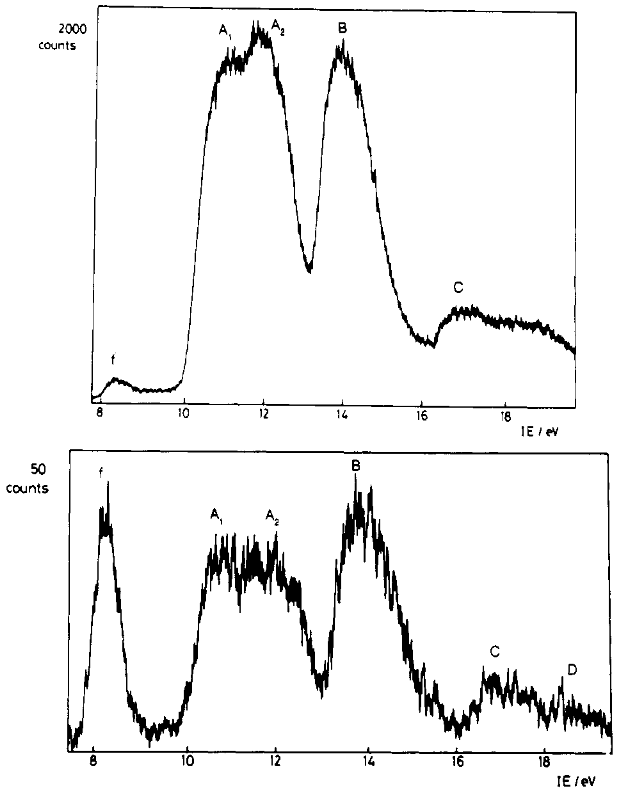

Figure 4. PE spectrum of $U(BH_3CH_3)_4$: upper, He I excitation; lower, He II excitation.

The spectrum of $Th(BH_4)_4$ shows one band (A) below 16 eV and another (C) with a well-defined shoulder (D) at higher IE. Apart from the absence of the f band, it closely resembles the spectrum of $U(BH_4)_4$.[5]

Discussion

The spectra of $M(BH_4)_4$ where M = Zr, Hf,[5,6] and U[5] have been reported previously. These two groups differ in their assignment of the lowest energy band. The spectrum of $Th(BH_4)_4$ was measured by us for completeness and as anticipated resembles

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(16) Beach, D. B.; Bomberi, K. D.; Edelstein, N. M.; Eisenberg, D. C.; Jolly, W. L.; Shinomoto, R.; Streitwieser, A., Jr. *Inorg. Chem.* **1986**, *25*, 1735.

Table I. Ionization Energy Data[b] for $M(BH_3CH_3)_4$ (M = Zr, Hf, Th, U) and $Th(BH_4)_4$[d]

	label	$Zr(BH_3CH_3)_4$	$Hf(BH_3CH_3)_4$		label	$Th(BH_3CH_3)_4$	$U(BH_3CH_3)_4$	label	$Th(BH_4)_4$
				M_{5f}	f		8.3		
$1t_1$[a]	A′	10.8	10.6	$3t_2$ $1t_1$	A_1	10.9	11.0	M_1	12.0
$3t_2$ $2a_1$ 1e $2t_2$	A	12.6	12.5	$2a_1$ 1e $2t_2$	A_2	11.8	11.8	M_2	13.0
	B	14.3[c]	14.2[c]		B	13.8[c]	13.9[c]		
$1t_2$	C	17.5	17.3	$1t_2$	C	16.8	16.9	C	17.5
$1a_1$	D	18.7	19.0	$1a_1$	D	18.2	18.3	D	18.5
C_{2s}	E	22.0	22.1	C_{2s}	E	22.2	22.0		
M_{4f}	f		24.7						

[a] Assignments for $M(BH_3CH_3)_4$ (M = Zr, Hf) based on calculations for $M(BH_4)_4$.[8] [b] All energy data in eV. [c] Ionization energies associated with C character of the $BH_3CH_3^-$ ligand. [d] In the spectra of $Th(BH_4)_4$ a He I β satellite of M and a He II β satellite of C appear at an apparent IE of 10 eV (see Figure 5).

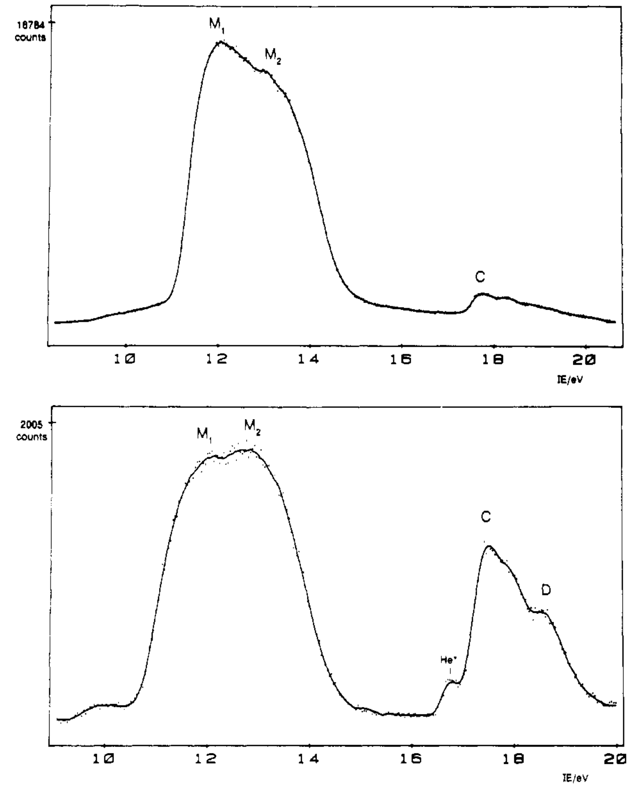

Figure 5. PE spectrum of $Th(BH_4)_4$: upper, He I excitation; lower, He II excitation.

that of the uranium rather than the zirconium and hafnium analogues. The main differences of the tetrakis(methyltrihydroborate) derivative PE spectra are the presence of extra bands (B and E) at ca. 14 and 22 eV and the shift of other bands (A, C, and D) to lower IE. Interestingly, the additional low-energy band found for the Zr and Hf tetrahydroborates at 11.6 eV is also present (at 10.6 and 10.8 eV) in the Zr and Hf tetrakis(methyltrihydroborates) (A′). Whatever the cause of this difference between the ionization behavior of the transition-metal and actinide tetrahydroborates it is not supressed by methyl substitution.

Band E at ca. 22 eV can be assigned to carbon 2s ionizations, and those between 16 and 20 eV (C and D) to the t_2 and a_1 boron 2s ionizations.

The profile of the principal ligand bands may be illuminated by comparison with the PE spectra of methane and ethane.[17] Whereas methane shows a broad Jahn–Teller split band between 13 and 16 eV associated with the t_2 ionization, ethane has two principal bands. The first one between 11 and 14 eV comprises the $1e_g$ ($\pi_{CH_3}{}^-$) and $3a_g$ (σ_{CC}) ionizations whereas that between 14 and 16.5 eV is assigned to the $1e_u$ ($\pi_{CH_3}{}^+$) ionization. In $BH_3CH_3^-$ it seems likely that the B–C σ ionizations will also lie in the lower IE band. Indeed, the intensity ratio of bands A and B, which is approximately 6:4, as is also found for ethane, suggests that this is the case. In considering the π ionizations it is reasonable to expect that boron character will predominate in the lower IE band (A) and carbon character in the upper of the two main bands (B). We therefore expect features associated with methyltrihydroborate complexing to be associated principally with the bands A and A′. The direct comparison of these bands with the principal bands of the tetrahydroborates is thus justified. Assignments for the observed ionization energies based on the preceding discussion and the results of Xα-SW calculations[8] are also given in Table I.

The differences between the transition-metal and actinide tetrahydroborates (and methyltrihydroborates) are worthy of comment. The principal difference is the separation of the low-energy band A′ from the main band A for Zr and Hf in both the unsubstituted tetrahydroborates and methyltrihydroborates. Three possible causes suggest themselves:

1. As Zr and Hf are smaller than Th and U, greater steric repulsion between the ligands could cause the t_1 level to rise. This is consistent with the assignment of Hitchcock et al.[6]

2. The mainly terminal B–H and B–C orbitals could have higher energies than the B–H–M bridging orbitals and be more differentiated in the "covalent" transition-metal complexes than in the "ionic" actinide complexes. This is the assignment of Downs et al.[5]

3. Zr and Hf have no valence orbital of t_1 symmetry whereas Th and U, being f-orbital elements, do. This would require the assignment of the HOMO in the d-block hydroborates to be t_1.[6]

The Xα-SW calculations support point 3.[8] One major difference in the theoretical results between the transition-metal tetrahydroborates and the actinide tetrahydroborates is the reversal of the bonding ligand HOMO from $1t_1$ in Zr and Hf tetrahydroborates to $3t_2$ in the actinide tetrahydroborates. The calculations suggest this reversal is due to a weaker interaction of the $3t_2$ orbital with the d metal orbitals and a small bonding interaction of the 5f orbitals with $1t_1$ ligand orbital for the actinide compounds. Thus, the $1t_1$ orbital is lowered in energy and $3t_2$ is raised in energy, leading to the single broad band A observed at ~11 eV in the actinide methyltrihydroborates (~12 eV in the actinide tetrahydroborates).

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Registry No. $Zr(BH_3CH_3)_4$, 86217-19-8; $Hf(BH_3CH_3)_4$, 97201-81-5; $Th(BH_3CH_3)_4$, 86238-35-9; $U(BH_3CH_3)_4$, 86217-20-1; $Th(BH_4)_4$, 12523-76-1.

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(17) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. *Molecular Photoelectron Spectroscopy*; Wiley-Interscience: London, 1970.