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# Molecular Structures of Two Metal Tetrakis(tetrahydroborates), $Zr(BH_4)_4$ and $U(BH_4)_4$: Equilibrium Conformations and Barriers to Internal Rotation of the Triply Bridging $BH_4$ Groups

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The molecular structures of $Zr[(\mu\text{-}H)_3BH]_4$ and $U[(\mu\text{-}H)_3BH]_4$ have been investigated by density functional theory (DFT) calculations and gas electron diffraction (GED). The triply bridged bonding mode of the tetrahydroborate groups in the former is confirmed, but both DFT calculations and GED structure refinements indicate that the $BH_4$ groups are rotated some 12° away from the orientation in which the three bridging B–H bonds are staggered with respect to the opposing $ZrB_3$ fragment. As a result the symmetry of the equilibrium conformation is reduced from $T_d$ to $T$. Bond distances and valence angles are as follows (DFT/GED): Zr–B = 232.2/232.4(5) pm; Zr–$H_b$ = 214.8/214.4(6) pm; B–$H_b$ = 125.3/127.8(8) pm; B–$H_t$ = 119.4/118.8(17) pm; $\angle ZrBH_b$ = 66.2/65.6(3)°; the smallest dihedral angle of type $\tau(BZrBH_b)$ = 48/45(2)°. DFT calculations on $Hf(BH_4)_4$ indicate that the structure of this molecule is very similar to that of the Zr analogue. Matrix-isolation IR spectroscopy and DFT calculations on $U(BH_4)_4$ show that while the polymeric solid-state structure is characterized by terminal triply bridging and metal–metal bridging bidentate $BH_4$ groups, all $BH_4$ groups are triply bridging in the gaseous monomer. Calculations with one of the two nonbonding 5f electrons on U occupying an $a_1$ and the other distributed equally among the three $t_2$ orbitals indicate that the equilibrium conformation has $T_d$ symmetry, i.e. that the three B–$H_b$ bonds of each tetrahydroborate group are exactly staggered with respect to the opposing $UB_3$ fragment with $\tau(BUBH_b)$ = 60°. Calculations including spin–orbit interactions indicate that Jahn–Teller distortions from $T_d$ symmetry are either absent or very small. The best agreement between observed and calculated GED intensity data was obtained for a model of $T_d$ symmetry, but models of $T$ symmetry with dihedral angles $\tau(BUBH_b) > 42°$ cannot be ruled out. Bond distances and valence angles are as follows (DFT/GED): U–B = 248.8/251.2(4) pm; U–$H_b$ = 227.7/231.5(6) pm; B–$H_b$ = 126.0/131.6(5) pm, B–$H_t$ = 119.5/117.8(11) pm; $\angle UBH_b$ = 65.6/63.1(3)°. It is suggested that the different equilibrium conformations of the three molecules are determined primarily by repulsion between bridging H atoms in different tetrahydroborate groups.

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## Introduction

Homoleptic tetrakis(tetrahydroborate) derivatives, $M(BH_4)_4$, of the heavier transition metals, e.g. M = Zr or Hf, and actinides, e.g. M = Th or U, are noteworthy on at least two counts. First, the combination of high-symmetry, efficient screening of the metal atom and the limited bridging ability of the $BH_4^-$ ligands results in remarkable volatility. This has led $U(BH_4)_4$, for example, to be considered as a means of separating uranium isotopes or processing uranium-containing materials.[1−3] Second, the structures pose several questions. (i) Given the variety of coordination modes and

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the fluxionality of the $BH_4^-$ ligands,[4,5] how exactly are these ligands linked to the metal center? (ii) How is the geometry of the $MB_4$ skeleton affected by the size of M or the presence of more or less nonbonding electrons [e.g. $5f^2$ for U(IV)]? (iii) How are the $BH_4^-$ ligands oriented with respect to one another and what sorts of barriers oppose their internal rotation or changes of the coordination mode?

The molecular structure of zirconium(IV) tetrakis(tetrahydroborate), $Zr(BH_4)_4$, was first determined by X-ray crystallography at −160 °C.[6] The compound was found to be monomeric in the solid phase with each tetrahydroborate group bonded to the metal atom through triple H bridges, $M[(\mu\text{-}H)_3BH]_4$. The positions of the bridging hydrogen atoms could not be determined with accuracy, but it was noted that the molecules occupy crystal sites of $T_d$ symmetry, which—barring disorder—implies that each $(\mu\text{-}H)_3BH$ group is oriented in such a manner that the three bridging B−H bonds are staggered with respect to the U−B bonds of the opposing $UB_3$ fragment. A neutron diffraction study of the hafnium analogue at 110 K showed that the crystal structures of $Hf(BH_4)_4$ and $Zr(BH_4)_4$ are isomorphous; there were no indications of disorder, and the bridging hydrogen atoms were located at positions corresponding to staggered $BH_4$ groups and molecular $T_d$ symmetry.[7] A subsequent gas electron diffraction study of $Zr(BH_4)_4$ showed that the molecule retains the $M[(\mu\text{-}H)_3BH]_4$ structure in the gas phase.[8] The thermal average orientation of the tetrahydroborate groups was, however, found to deviate from the staggered, and the symmetry of the average structure was consequently $T$ rather than $T_d$. Since no corrections were made for thermal motion, the apparent symmetry lowering may be due to large-amplitude librational motion of the tetrahydroborate groups rather than distortion of the equilibrium structure. Subsequent careful studies of the IR and Raman spectra failed to settle unequivocally whether the equilibrium structure of $Zr(BH_4)_4$ has $T$ or $T_d$ symmetry.[9,10]

A single-crystal X-ray diffraction study of uranium(IV) tetrakis(tetrahydroborate), $U(BH_4)_4$, published by Bernstein and co-workers[11] 30 years ago, showed that this compound is associated in the solid state; each uranium atom is surrounded by six boron atoms in an approximately octahedral arrangement. Two boron atoms (in cis positions) were found at a distance of 253 pm from the uranium atom, while the remaining four were approximately equidistant from two metal atoms with an average U−B distance of 287 pm. The positions of H atoms were determined in a later investigation by neutron diffraction:[12] the two B atoms at the shorter distance belong to terminal $BH_4$ groups bonded to the metal atom through triple H bridges, while the four B atoms at the longer distance belong to bridging $BH_4$ groups bonded to each of the two metal atoms through double H bridges. Each uranium atom is thus surrounded by *fourteen* bridging hydrogen atoms. Several years later, Charpin and co-workers described a second crystalline form in which the U atom and the B atoms of the four bridging, bidentate $BH_4$ groups are coplanar, while the terminal, tridentate $BH_4$ groups occupy trans positions.[13]

Despite its polymeric crystal structure, $U(BH_4)_4$ vaporizes at near-ambient temperatures. On the evidence of molecular weight[14] and mass spectrometric[15] measurements, the vapor consists of monomeric $U(BH_4)_4$ molecules. Similarities in the IR spectra of $U(BH_4)_4$ and $Zr(BH_4)_4$ vapors have been taken to imply that the two molecules have analogous structures in the gas phase,[9,10,15,16] and the same inference has been drawn from the UV photoelectron spectra of the gaseous molecules $M(BH_4)_4$, where M = Zr, Hf, or U.[17] A slightly different view comes from the optical spectra of molecular crystals of $Hf(BH_4)_4$ doped with $U(BH_4)_4$, which have been interpreted[18] on the basis of discrete $U(BH_4)_4$ molecules with overall $T_d$ symmetry.

The coordination of $BH_4^-$ is a matter of some relevance to the activation of the isoelectronic but much less basic $CH_4$ molecule.[19] That the issue is far from straightforward, however, is demonstrated by the discovery that the crystal structures of $U(BH_4)_4$[11−13] and several other tetrahydroborates, e.g. $Ti(BH_4)_3(PMe_3)_2$,[19] reveal molecular units in which the metal atom is surrounded by $BH_4^-$ groups linked to it through different coordination modes. In view of this and other uncertainties, closer examination of $U(BH_4)_4$ vapor appeared warranted to establish the structure of the gaseous monomer. At the same time, differences in the size and electronic makeup of Zr(IV) and U(IV) (with its two 5f electrons) urged a comparison of $U(BH_4)_4$ with $Zr(BH_4)_4$. Accordingly we present the results (i) of quantum chemical density functional theory (DFT) calculations for the three molecules $Zr(BH_4)_4$, $Hf(BH_4)_4$, and $U(BH_4)_4$ and (ii) of a new gas electron diffraction study of $Zr(BH_4)_4$ plus the first

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such study of $U(BH_4)_4$. The calculations indicate that the equilibrium conformations of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ have $T$ rather than $T_d$ symmetry, a conclusion confirmed by the GED structure refinement. By contrast, calculations and experiment favor $T_d$ symmetry for $U(BH_4)_4$.

## Density Functional Theory Calculations

The DFT calculations on $M(BH_4)_4$, M = Ti, Zr, Hf, or U, were carried out using the ADF program system developed by Baerends et al.[20,21] Orbitals were described by Slater type orbital (STO) basis sets. The frozen core approximation was used for all atoms except H. For B the 1s orbital was kept frozen in its atomic shape. For Ti the orbitals were frozen up to and including 2p, for Zr up to and including 3d, for Hf up to and including 4f, and for U up to and including 5d. The number of unfrozen basis functions, in order of increasing angular momentum, was (2,1) for H, (2,2,1) for B, (5,3,3) for Ti, (5,4,3) for Zr, (5,4,3,1) for Hf, and (4,3,3,3) for U, thus yielding basis sets of TZV quality for the metal atoms and of DZVP quality for B and H. Slater exchange and the Vosko−Wilk−Nusair parametrization of the LDA correlation energy,[22] with the gradient correction of Becke[23] for exchange and of Perdew[24] for correlation, were used for the exchange-correlation energies. Most calculations were carried out with the accuracy of numerical integrations set to $10^{-6.5}$ for each integral.[21] This is believed to give a numerical noise less than 0.5 kJ $mol^{-1}$ in the final energies. Calculation of the force field of the $T_d$ model of $U(BH_4)_4$ and the search for possible Jahn−Teller distorted structures were, however, carried out with an accuracy of $10^{-9.5}$.

Exploratory structure optimizations were carried out with an earlier version of the ADF program (Release 2.3.0) and relativistic effects taken into account through the quasi-relativistic Pauli formalism.[25] The final results quoted in this article were, however, all obtained with the 2000.02 Release and the zero-order regular approximation (ZORA).

Force constants were calculated numerically from analytical gradients. Vibrational frequencies, root-mean-square amplitudes of vibration, $l$, and vibrational correction terms, $D = r_a - r_{\alpha¢}$, were calculated by the program ASYM40.[26]

## Experimental Section

**Syntheses.** Zirconium tetrakis(tetrahydroborate), $Zr(BH_4)_4$, was prepared by the reaction between $LiBH_4$ and $ZrCl_4$ in the absence of a solvent, broadly in accordance with the procedure described by Wallbridge et al.[27] Freshly recrystallized, finely ground $LiBH_4$ (2.20 g, 110 mmol, *ex* Aldrich) and $ZrCl_4$ (3.75 g, 16.2 mmol, *ex* Aldrich) were mixed gently under vacuum until reaction occurred (after about 10 min) with the evolution of heat and the formation of what appeared to be a sticky white mass. The mixture was then stirred for 1 h at room temperature with the aid of a glass-coated magnetic “flea”. After cooling to 77 K, any noncondensable gas was removed; the reaction mixture was then warmed to room temperature under continuous pumping through a trap cooled to 163 K where the $Zr(BH_4)_4$ condensed as a white solid. The crude product was purified by revaporization at 273 K and trapping at 195 K. The yield (1.8 g, 12.0 mmol) was 75% of that based on quantitative conversion of the $ZrCl_4$ taken. After the purity of the sample had been checked by reference to its IR spectrum,[4,5,27] the material was stored until needed in evacuated Pyrex glass ampules each equipped with a break seal.

Uranium tetrakis(tetrahydroborate), $U(BH_4)_4$ was prepared in a novel manner by solid-state metathesis between $UCl_4$ (*ex* BNFL) and a 2- to 10-fold excess of freshly recrystallized $LiBH_4$ (*ex* Aldrich). The finely ground solids, together with some glass beads, were introduced into a Pyrex glass reaction vessel closed by a greaseless (Young’s) valve and connected to an all-glass train of U-traps. Mixing of the powders in the evacuated apparatus ($P < 10^{-4}$ Torr) was achieved by the slow stirring action of a glass-coated magnetic flea. The mixture was allowed to react for up to 2 weeks at room temperature, the volatile products being fractionated in vacuo. The purity of the sample was checked by reference to the IR spectrum of an annealed solid film at 77 K.[13]

**Spectroscopic Measurements.** The IR spectra of $Zr(BH_4)_4$ and $U(BH_4)_4$ in the solid and matrix-isolated states were measured in the region 400−4000 $cm^{-1}$ with a Mattson “Galaxy” or a Nicolet “Magna” 560 FT-IR spectrometer. Solid Ar or $N_2$ matrixes doped with these molecules, typically at dilutions estimated to be ca. 1:200, were prepared by continuous deposition of the tetrahydroborate vapor with an excess of the matrix gas on a CsI window cooled to ca. 12 K by means of a Displex closed-cycle refrigerator (Air Products Model CS 202). Solid films of the tetrahydroborates were analyzed by causing the vapor to condense on a CsI window contained in an evacuated shroud and maintained at 77 K.

**Gas Electron Diffraction.** The gas electron diffraction data for $Zr(BH_4)_4$ and $U(BH_4)_4$ were recorded on the Baltzers KDG2 unit at the University of Oslo[28] with a metal inlet system at 22 ± 2 (Zr) or 62−65 °C (U) and nozzle-to-plate distances of approximately 50 and 25 cm. The scattering pattern of $Zr(BH_4)_4$ was recorded on Fuji Imaging Plates BAS-III (three plates for each nozzle-to-plate distance) and scanned on a Fujifilm BAS 1800 II imaging plate reader. The relative intensity data were processed using a program written by S. Samdal, D. J. Shorokhov, and T. G. Strand.[29] The scattering pattern of $U(BH_4)_4$ was recorded on Kodak Electron Image Plates; six plates from each distance were scanned on an Agfa Arcus II scanner and the data processed as described elsewhere.[30] Atomic scattering factors were taken from ref 31. Backgrounds were drawn as least-squares adjusted polynomials to the difference between the total experimental and calculated

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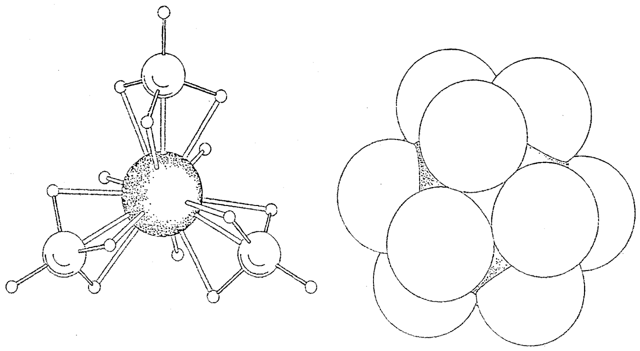

**Figure 1.** Left: Ball-and-stick molecular model of $Zr(BH_4)_4$, symmetry *T*. Right: Space-filling model showing the Zr and twelve bridging H atoms. Program Pluton.[33]

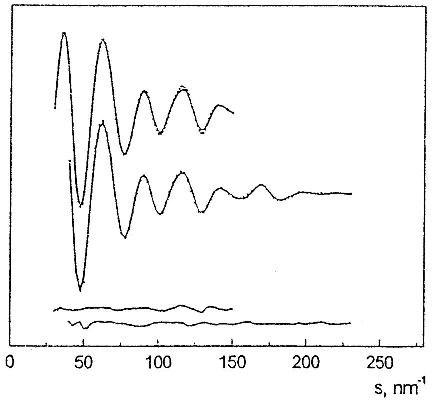

**Figure 2.** Above: Experimental (dots) and calculated (line) modified molecular intensity curves for $Zr(BH_4)_4$. The vertical scale is arbitrary. Below: Difference curves.

molecular intensities. Structure refinements by least-squares calculations on the molecular intensities were carried out using the program KCED 26 written by G. Gundersen, S. Samdal, H. M. Seip, and T. G. Strand. The calculated intensity contained terms for all interatomic distances including nonbonded H···H distances. Since the refinements had been carried out with diagonal weight matrixes, the estimated standard deviations listed in Tables 1 and 2 have been multiplied by a factor of 2.5 to include uncertainty due to data correlation[32] and expanded to include a scale uncertainty of 0.1%.

Structure refinements of $Zr(BH_4)_4$ were based on a molecular model of *T* symmetry (see Figure 1) characterized by five independent structure parameters, viz. the M−B bond distances, the terminal and bridging B−H distances, $B-H_t$ and $B-H_b$, the valence angle $\angle H_tBH_b$, and the torsional angle $\tau(BMBH_b)$. The five independent structure parameters were refined along with the six root-mean-square vibrational amplitudes indicated in Table 1. The final structure refinements of $U(BH_4)_4$ were based on a model of $T_d$ symmetry. Four structure parameters were refined along with the six root mean square vibrational amplitudes indicated in Table 4.

Calculated and observed intensity curves and radial distribution curves are compared in Figures 2−5. We consider the agreement satisfactory.

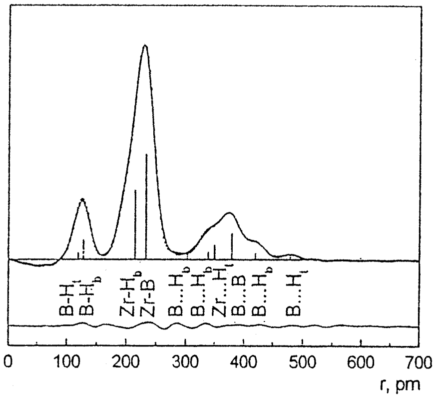

**Figure 3.** Experimental (dots) and calculated (line) radial distribution curves for $Zr(BH_4)_4$. The vertical scale is arbitrary. Major interatomic distances are indicated by bars of height approximately proportional to the area under the corresponding peak. Artificial damping constant $k = 0.12$ pm$^2$.

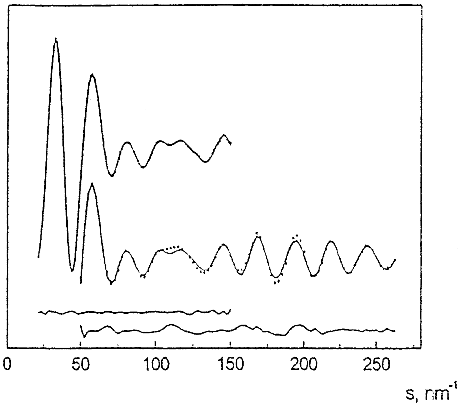

**Figure 4.** Above: Experimental (dots) and calculated (line) modified molecular intensity curves for $U(BH_4)_4$. The vertical scale is arbitrary. Below: Difference curves.

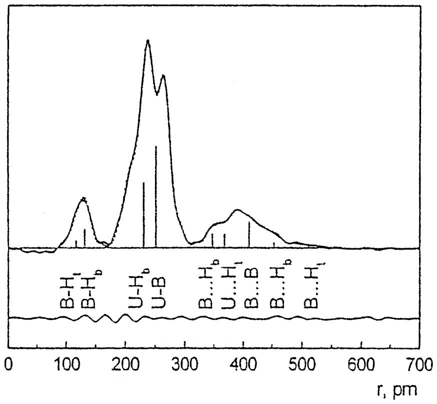

**Figure 5.** Experimental (dots) and calculated (line) radial distribution curves for $U(BH_4)_4$. The vertical scale is arbitrary. Major interatomic distances are indicated by bars of height approximately proportional to the area under the corresponding peak. Artificial damping constant $k = 0.12$ pm$^2$.

## Results and Discussion

**Zirconium Tetrakis(tetrahydroborate).** The ADF program allows structure optimization under $T_d$ but not under *T* symmetry. Structure optimization of $Zr(BH_4)_4$ without imposition of symmetry, however, converged to a model of *T* symmetry with the structure parameters listed in Table 1. Calculation of the molecular force field followed by normal

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**Table 1.** Interatomic Distances ($r$), Root Mean Square Vibrational Amplitudes ($l$), Valence Angles, and Torsional Angles in $Zr(BH_4)_4$ Obtained by Density Functional Theory (ADF-ZORA) Calculations or Gas Electron Diffraction (GED)[a]

|  | ADF-ZORA |  | GED |  |
|---|---|---|---|---|
| symmetry | $T$ |  | $T$ |  |
|  | Bond Distances |  |  |  |
|  | $r_e$ | $l$ | $r_a$ | $l$ |
| Zr−B | 232.2 | 5.8 | 232.4(5) | 7.1(4) |
| $Zr-H_b$ | 214.8 | 14.0 | 214.4(6) | 14.8(13) |
| $B-H_b$ | 125.3 | 9.1 | 127.8(8) | [9.1] |
| $B-H_t$ | 119.4 | 8.3 | 118.8(17) | [8.3] |
|  | Nonbonded Distances |  |  |  |
|  | $r_e$ | $l$ | $r_a$ | $l$ |
| $Z\cdots H_t$ | 351.6 | 9.6 | 350(2) | 15(3) |
| $B\cdots B$ | 379.1 | 11.7 | 379(1) | 11.3(12) |
| $B\cdots H_b$ | 307.8 | 20.3 | 303(2) | [20.3] |
| $B\cdots H_b$ | 335.3 | 21.0 | 339(2) | [21.0] |
| $B\cdots H_b$ | 421.1 | 14.8 | 420(1) | 12(2) |
| $B\cdots H_t$ | 481.5 | 16.8 | 479(2) | 18(3) |
|  | Valence Angles |  |  |  |
|  | $\angle_e$ |  | $\angle_\alpha$ |  |
| $<ZrBH_b$ | 66.2 |  | 65.6(3) |  |
| $<H_bBH_b$ | 104.8 |  | 104.2(4) |  |
| $<H_bBH_t$ | 113.8 |  | 114.4(3) |  |
|  | Torsional Angle |  |  |  |
|  | $\tau_e$ |  | $\tau_\alpha$ |  |
| $\tau(BZrBH_b)$ | 48.2 |  | 45(2) |  |
| $R$-factor[b] |  |  | 0.036 |  |

[a] Interatomic distances and vibrational amplitudes in picometers, angles in degrees. Estimated standard deviations in parentheses in units of the last digit. Nonrefined amplitudes in square brackets. [b] $R = \sqrt{[Sw(I_{obs} - I_{calc})^2/Sw(I_{obs})^2]}$.

coordinate analysis yielded only real vibrational frequencies, thus confirming that this structure corresponds to a minimum on the potential energy hypersurface. The smallest torsional angle of type $\tau(BZrBH_b)$ is calculated to be 48°. If this angle is 60°, each tetrahydroborate group is oriented in such a way that the three $B-H_b$ bonds are staggered with respect to the opposing $ZrB_3$ fragment, and the molecular symmetry is $T_d$. In the following we shall refer to this conformation as $T_d$ (stag). If the torsional angle is 0°, the three $B-H_b$ bonds of each tetrahydroborate group are eclipsing the opposing Zr−B bonds, and the symmetry will again be $T_d$. We shall refer to this conformation as $T_d$ (ecl). The calculations thus yield an equilibrium conformation of $Zr(BH_4)_4$, which is closer to staggered than eclipsed. The lowest vibrational mode (183 $cm^{-1}$) involves concerted internal libration of the ($\mu$-$H_3BH$) groups about the Zr−B bond axes under retention of molecular $T$ symmetry.

Least-squares structure refinement of a model of $T$ symmetry to the gas electron diffraction data yielded structure parameters in very good agreement with the calculated ones (see Table 1). In particular the torsional angle, which has been corrected for thermal motion, was found to be 45(2)°, i.e. significantly smaller than 60°. When structure refinements were carried out on a staggered $T_d$ model, the $R$-factor increased from 3.6 to 4.5% corresponding to an $R$-factor ratio of $R = 1.25$. The use of Hamilton's $R$-factor ratio test[34] confirmed that the $T_d$ model may be rejected at the 99.5% confidence level. Thus both calculation and experiment indicate that the equilibrium structure has $T$ rather than $T_d$ symmetry.

The barrier to concerted rotation of the four $BH_4$ groups into a staggered orientation was estimated by optimizing a $T_d$(stag) model. The barrier thus obtained was $V(60°) = 1.0$ kJ $mol^{-1}$. The energy difference is so small that intermolecular forces well may lead to a $T_d$ molecular structure in the crystalline phase.

The energy required to rotate *one* $BH_4$ group into an eclipsed orientation was estimated by optimizing a molecular model with three staggered and one eclipsed $BH_4$ group and overall $C_{3v}$ symmetry. The rotational barrier thus obtained was 13.9 kJ $mol^{-1}$. Optimization of a $T_d$ (ecl) model yielded a barrier to concerted rotation of the *four* $BH_4$ groups into eclipsed orientations of $V(0°) = 123$ kJ $mol^{-1}$, more than *eight* times larger than the barrier to rotation of one group. What is the origin of these barriers? In Figure 1 we present a space-filling model of Zr and the twelve bridging H atoms. It is seen that each bridging H atom is in van der Waals contact with two bridging H atoms in neighboring $BH_4$ groups. The distance between them is $H_b\cdots H_b = 235$ pm, slightly shorter than the sum of their van der Waals radii, 240 pm,[35] thus indicating a slightly repulsive interaction. The total number of such short $H_b\cdots H_b$ contacts in the molecule is twelve. Concerted internal rotation of the $BH_4$ groups by 12° to bring them into a perfectly staggered $T_d$ orientation reduces these twelve distances to 231 pm, while the energy of the molecule increases by 1.0 kJ $mol^{-1}$. We suggest, therefore, that the barrier to concerted rotation is due to a slightly increased van der Waals repulsion between bridging H atoms.

Rotation of *one* $BH_4$ group into an eclipsed orientation yields a $C_{3v}$ structure also characterized by twelve short $H_b\cdots H_b$ contacts. Nine of these distances are indistinguishable from those of the $T_d$ (stag) model, while three have been reduced by about 7 pm to 225 pm. The reduction of these distances is hardly sufficient to explain an energy increase of 13.9 kJ $mol^{-1}$. We suggest that the energy increase is due to an inherent, electronic barrier to internal rotation of the $BH_4$ group. Concerted rotation of the *four* tetrahydroborate groups into eclipsed orientations yields a model characterized by six very short $H_b\cdots H_b$ contacts at 178 pm, and the energy rises to 123 kJ $mol^{-1}$ above the equilibrium conformation. We suggest that half of this energy barrier, $4 \times 13.9$ kJ $mol^{-1}$ or about 56 kJ $mol^{-1}$, is due to the inherent barriers to internal rotation of the four $BH_4$ groups, while the remainder is due to increased repulsion between bridging hydrogen atoms.

If this suggestion is correct, the rotational barriers at the $T_d$ staggered and eclipsed conformations should increase if the Zr atom is replaced by a smaller atom like Ti. We decided, therefore to carry out similar ADF calculations on the model compound $Ti(BH_4)_4$.[36,37] The results are summarized in Table 2; the equilibrium conformation of $Ti(BH_4)_4$

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(34) Hamilton, W. C. *Statistics in Physical Science*; The Ronald Press Co.: New York, 1964; pp 157−162 and 216−222. The number of observed intensity values is 174. These values are correlated, and we assumed them to be equivalent to 174/2.5 = 70 independent observations.[32] The number of refined parameters (including two scale factors) was 15, and the dimension of the hypothesis one.

(35) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

**Table 2.** Molecular Conformations of $M[(\mu\text{-}H)_3BH]_4$, M = Ti, Zr, or Hf; Dihedral Angles (deg), Relative Energies (kJ mol$^{-1}$), and M−B Bond and Shortest Distances (pm) between Bridging H Atoms in Different Tetrahydroborate Groups Obtained by DFT Calculations

| M | symmetry(conformn) | $\tau(BMBH_b)$ | $\Delta E$ | M−B | $H_b\cdots H_b$ |
|---|---|---|---|---|---|
| Ti | $T$ | 47 | 0 | 217 | 12 × 212 |
| Ti | $T_d$ (stag) | 60 | 2.7 | 217 | 12 × 206 |
| Ti | $C_{3v}$ | 3 × 60; 1 × 0 | 24.6 | 3 × 218; 1 × 218 | 6 × 209; 3 × 203; 3 × 206 |
| Ti | $T_d$ (ecl) | 0 | 195 | 224 | 6 × 162; 24 × 312 |
| Zr | $T$ | 48 | 0 | 232 | 12 × 235 |
| Zr | $T_d$ (stag) | 60 | 1.0 | 232 | 12 × 231 |
| Zr | $C_{3v}$ | 3 × 60; 1 × 0 | 13.9 | 3 × 232; 1 × 233 | 6 × 231; 3 × 225; 3 × 232 |
| Zr | $T_d$ (ecl) | 0 | 123 | 236 | 6 × 178; 24 × 326 |
| Hf | $T$ | 47 | 0 | 231 | 12 × 237 |
| Hf | $T_d$ (stag) | 60 | 2.7 | 232 | 12 × 231 |
| Hf | $C_{3v}$ | 3 × 60; 1 × 0 | 15.5 | 3 × 232, 1 × 232 | 6 × 231; 3 × 226; 3 × 232 |
| Hf | $T_d$ (ecl) | 0 | 129 | 236 | 6 × 178; 24 × 327 |

**Table 3.** Bond Distances (pm) and Valence and Torsional Angles (deg) in $Hf(BH_4)_4$ Obtained by Density Functional Theory (ADF-ZORA) Calculations or Single Crystal Neutron Diffraction at 110 K

| symmetry | ADF-ZORA[a] $T$ | neutron diffraction[b] $T_d$ |
|---|---|---|
| | Bond Distances | |
| Hf−B | 231.5 | 228.1(8) |
| $Hf-H_b$ | 215.5 | 213.0(9) |
| $B-H_b$ | 125.2 | 123.5(10) |
| $B-H_t$ | 119.2 | 115.0(19) |
| | Valence Angles | |
| $\angle HfBH_b$ | 66.8 | 67.1(5) |
| $\angle H_bBH_b$ | 105.5 | 105.8(6) |
| $\angle H_bBH_t$ | 113.2 | 112.9(10) |
| | Torsional Angle | |
| $\tau(BHfBH_b)$ | 47.4 | 60.0[c] |

[a] This work. [b] Reference 2. Uncorrected for thermal motion. [c] Determined by the space group.

is calculated to be very similar to that of $Zr(BH_4)_4$, in particular with torsional angle $\tau(BTiBH_b) = 47°$. The M−B bond distance is, however, about 15 pm shorter than in the Zr compound, and the distances between H atoms in neighboring $BH_4$ groups are consequently reduced by about 20 pm to 212 pm. The barrier to concerted rotation of four tetrahydroborate groups into staggered orientations is increased from 1.0 to 2.7 kJ mol$^{-1}$, and the barrier to concerted rotation into eclipsed orientations from 123 to 195 kJ mol$^{-1}$.

**Hafnium Tetrakis(tetrahydroborate).** Structure optimization of $Hf(BH_4)_4$ converged to a model of $T$ symmetry and the structure parameters listed in Table 3. Comparison of bond distances in the tetrahalides $MX_4$, M = Zr or Hf; X = F, Cl, Br or I, suggests that, as a result of the well-known lanthanide contraction[38] and relativistic effects,[39] the bonding radius of Hf is marginally (between 0 and 2 pm) smaller than that of Zr,[40] and Hf−B distances are indeed calculated to be marginally shorter than the Zr−B distances in $Zr(BH_4)_4$. The structures of the tetrahydroborate groups in the two compounds are also very similar; bond distances differ by less than 1 pm and valence angles by less than a degree. The dihedral angles $\tau(BMBH_b)$ also differ by less than 1°, as is to be expected if the orientation is determined by repulsion between bridging hydrogen atoms. The calculated barriers to concerted rotation of four $BH_4$ groups into staggered orientations differ by about 2 kJ mol$^{-1}$ and the barriers to rotation into eclipsed orientations by 6 kJ mol$^{-1}$, the barriers of the hafnium compound being the larger in both cases (see Table 2).

The agreement between calculated bond distances and valence angles and those obtained by neutron diffraction at 110 K[7] is as close as is to be expected considering that the latter have not been corrected for thermal motion (see Table 3). However, while the calculations indicate that the equilibrium symmetry is $T$, the neutron diffraction study indicates the molecular structure in the solid state to be $T_d$. Since the calculations indicate that rotation of the $BH_4$ groups into staggered orientations requires no more than about 3 kJ mol$^{-1}$, the orientations adopted in the crystalline phase may well be determined by intermolecular forces.

**Uranium Tetrakis(tetrahydroborate).** While $Zr(BH_4)_4$ and $Hf(BH_4)_4$ are closed shell molecules, $U(BH_4)_4$ contains two nonbonding electrons in 5f atomic orbitals on the metal atom. These electrons are expected to enter different f-orbitals with parallel spins to yield a triplet electronic ground state. Density functional theory calculations without spin−orbit coupling were therefore carried out on triplet states, with a set of separate Kohn−Sham orbitals for each spin.

Exploratory structure optimizations were carried out with a start model with two bidentate and two tridentate tetrahydroborate groups, i.e. on $U[(\mu\text{-}H)_2BH_2]_2[(\mu\text{-}H)_3BH]_2$, as well as on a start model with one bidentate and three tridentate groups; i.e. on $U[(\mu\text{-}H)_2BH_2][(\mu\text{-}H)_3BH]_3$. When structure optimizations were carried out without symmetry restrictions, the bidentate $BH_4$ groups rotated into tridentate bonding modes. The IR spectra of the matrix isolated molecule (see below) confirm that the equilibrium structure of the molecule indeed is characterized by *four* tridentate tetrahydroborate groups.

When structure optimization was continued with four tridentate tetrahydroborate groups, the structure approached $T_d$ symmetry, but did not converge. A molecular field of $T_d$ symmetry splits the 5f manifold into one nondegenerate orbital of $a_1$ and two triply degenerate sets of $t_1$ and $t_2$

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(36) To the best of our knowledge, $Ti(BH_4)_4$ has never been prepared and may not exist under normal conditions. Thus the reaction of $TiBr_4$ with $LiBH_4$ gives $Ti(BH_4)_3$ rather than $Ti(BH_4)_4$.[37]

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(38) Kaltsoyannis, N.; Scott, P. *The f Elements*; Oxford University Press: Oxford, U.K., 1999.

(39) Pyykkö, P.; Snijders, J. G.; Baerends, E. J. *Chem. Phys. Lett.* **1981**, *83*, 432.

(40) Hargittai, M. *Chem. Rev.* **2000**, *100*, 2233.

**Table 4.** Interatomic Distances ($r$), Root Mean Square Vibrational Amplitudes ($l$), Valence Angles, and Torsional Angles in $U(BH_4)_4$ Obtained by Density Functional Theory (ADF-ZORA) Calculations or Gas Electron Diffraction (GED)[a]

| | ADF-ZORA | | GED | |
|---|---|---|---|---|
| symmetry | $T_d$ | | $T_d$ | |
| Bond Distances | | | | |
| | $r_e$ | $l$ | $r_a$ | $l$ |
| U−B | 248.8 | 6.2 | 251.2(4) | 7.0(3) |
| $U-H_b$ | 227.7 | 13.6 | 231.5(6) | 17.3(10) |
| $B-H_b$ | 126.0 | 9.2 | 131.6(5) | [9.2] |
| $B-H_t$ | 119.5 | 8.4 | 117.8(11) | [8.4] |
| Nonbonded Distances | | | | |
| | $r_e$ | $l$ | $r_a$ | $l$ |
| $U\cdots H_t$ | 368.4 | 9.9 | 368(1) | 8.9(14) |
| $B\cdots B$ | 406.4 | 18.5 | 409(1) | 15.9(17) |
| $B\cdots H_b$ | 345.7 | 42.1 | 347(5) | [42.1] |
| $B\cdots H_b$ | 447.5 | 16.3 | 445(1) | 14(3) |
| $B\cdots H_t$ | 508.7 | 24.3 | 507(1) | 24(4) |
| Valence Angles | | | | |
| | $\angle_e$ | | $\angle_\alpha$ | |
| $\angle UBH_b$ | 65.6 | | 63.1(3) | |
| $\angle H_bBH_b$ | 104.1 | | 101.1(4) | |
| $\angle H_bBH_t$ | 114.4 | | 116.9(3) | |
| Torsional Angle | | | | |
| | $\tau_e$ | | $\tau_\alpha$ | |
| $\tau(BUBH_b)$ | 60 | | [60][b] | |
| $R$-factor | | | 0.034 | |

[a] Interatomic distances and vibrational amplitudes in picometers, angles in degrees. Estimated standard deviations in parentheses in units of the last digit. Nonrefined parameters in square brackets. [b] See comment in text.[c] $R = \upsilon[Sw(I_{obs} - I_{calc})^2/Sw\ (I_{obs})^2]$.

symmetry. One nonbonding electron was found to occupy the 5f $a_1$ orbital, the other flitted from one 5f $t_2$ orbital to another.

$U(BH_4)_4$ with $T_d$ symmetry and the f-electron configuration $a_1^1t_2^1$ is orbitally degenerate and may be subject to Jahn−Teller distortion. We shall return to this question below. For the moment we solved the convergence problem by continuing the calculations under $T_d$ symmetry and the $t_2$ electron distributed equally between the three degenerate orbitals. (Population analysis of the optimized wave function indicates that the $t_2$ orbitals have 96% U f-character, while the $a_1$ orbital has 90% U f- and 6% U s-character). The optimized structure parameters are listed in Table 4. Calculation of the molecular force field and normal coordinate analysis yielded no imaginary frequencies and thus confirmed that the $T_d$ structure represents a minimum on the potential energy hypersurface (at this computational level). The lowest vibrational mode (46 $cm^{-1}$) is of $a_2$ symmetry and involves concerted internal rotation of the tetrahydroborate groups. The barrier to concerted internal rotation of the four $BH_4$ groups into eclipsed orientations is calculated to be 49 kJ $mol^{-1}$, less than one-half of the corresponding barrier in the Zr analogue.

Comparison of the bond distances in $ZrCl_4$ and $UCl_4$ indicates that the bonding radius of U is about 18 pm larger than that of Zr,[40] and the U−B distance is indeed calculated to be 17 pm longer than the Zr−B distance. As a consequence the shortest distances between bridging H atoms in different tetrahydroborate groups in $U(BH_4)_4$ (255 pm) are longer than the sum of their van der Waals radii (240 pm); even for the $T_d$(stag) conformation; there is no need for distortion of this conformation in order to reduce van der Waals repulsion.

Structure optimizations under $T_d$ symmetry were also carried out for the singly excited states with the 5f-electron configurations $t_2^2$, $a_1^1t_1^1$, or $t_2^1t_1^1$. Calculations with $t_1$ or $t_2$ electrons distributed equally over the three degenerate orbitals yielded energies 39, 55, and 102 kJ $mol^{-1}$, respectively, above that of the $a_1^1t_2^1$ configuration. See Table 5. Even though spin−orbit coupling reduced the relative energy of the $t_2^2$ configuration to 21 kJ $mol^{-1}$, we believe these energies to be too high for molecules in excited electronic states to be present in detectable quantities at the temperature of our GED experiment (about 340 K).

Finally we explored possible Jahn−Teller (J−T) distortions of the $T_d$ structure with the ground state $a_1^1t_2^1$ electron configuration.[41] Distortion along an e vibrational mode yields an elongated or compressed tetrahedral structure of $D_{2d}$ symmetry. At the same time the $t_2$ f-orbitals are split into a nondegenerate orbital of $b_2$ and two degenerate orbitals of e symmetry. Structure optimization converged to a slightly compressed tetrahedral structure with the electron configuration $a_1^1b_2^1$.[42] The energy was 12.8 kJ $mol^{-1}$ below that calculated for the $T_d$ structure.[43] Examination of the optimal $D_{2d}$ structure showed that the deformations from $T_d$ symmetry were very small: two ∠BUB valence angles were increased by less than 1°, while the remaining four were decreased by less than 0.5°. $UBH_b$ and HBH valence angles were all changed by less than 1°. Such distortions are surely too small to be detected by GED.

The Jahn−Teller $T_d$ to $D_{2d}$ distortion energy obtained at the DFT computational level is so small that we decided to investigate the effect of spin−orbit coupling. Combination of the $a_1$ f-orbital of the $T_d$ structure with the appropriate spin functions ($\alpha$ or $\beta$) gives a pair of degenerate spin−orbitals of $e_{1/2}$ symmetry, while spin−orbit coupling splits the 6-fold degenerate spin−orbitals based on the $t_2$ f-orbitals into a quadruply degenerate $u_{3/2}$ and a doubly degenerate $e_{5/2}$ orbital. Single point calculations on the optimized $T_d$ model indicated that the most stable electron configuration is $e_{1/2}^1u_{3/2}^1$, while a single point calculation on the optimized $D_{2d}$ structures indicated that the most stable electron configuration is $e_{1/2}^1e_{3/2}^1$ (where $e_{1/2}$ and $e_{3/2}$ refer to the irreducible representations of the group $D_{2d}$*). The calculations including spin−orbit coupling indicate that the energy of the $D_{2d}$ structure is 4.5 kJ $mol^{-1}$ *higher* than that of the $T_d$ structure. See Table 5.

Distortion of the $T_d$ structure along a $t_2$ vibrational mode yields a trigonal pyramidal structure of $C_{3v}$ symmetry. At the same time the $t_2$ f-orbitals are split into a nondegenerate orbital of $a_1$ and two degenerate orbitals of e symmetry. Structure optimization without spin−orbit coupling con-

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(41) Jotham, R. W.; Kettle, S. F. A. *Inorg. Chim. Acta* **1971**, *5*, 183.

(42) A $D_{2d}$ structure with the electron configuration $a_1^1e^1$ would be orbitally degenerate and thus subject to further J−T distortion to $D_2$ or $C_{2v}$ symmetry.[41] These possibilities were not explored.

(43) Calculation of the molecular force field for the $D_{2d}$ structure with the $a_1^1b_2^1$ electron configuration was thwarted by SCF convergence problems for distorted geometries.

**Table 5.** Molecular Symmetry and Conformations of $U(BH_4)_4$, Electron Configurations, Binding (*E*) or Relative Energies (*DE*) (kJ $mol^{-1}$) and Number of Imaginary Frequencies ($n_{imag}$) Obtained by Calculations at the ADF-ZORA and ADF-ZORA + Spin−Orbit (SO) Coupling Computational Levels

| | ADF-ZORA | | | ADF-ZORA + SO | |
|---|---|---|---|---|---|
| symmetry (conformn) | config | $E/\Delta E$ | $n_{imag}$ | config | $E/\Delta E$ |
| $T_d$ (stag) | $a_1{}^1t_2{}^1$ | $E = -8825.0$<br>($\Delta E = 0$) | 0 | $e_{1/2}{}^1u_{3/2}{}^1$ | $E = -8907.0$<br>($\Delta E = 0$) |
| $T_d$ (ecl) | $a_1{}^1t_2{}^1$ | $\Delta E = +48.6$ | 1 | $e_{1/2}{}^1u_{3/2}{}^1$ | $\Delta E = +46.8$ |
| $C_{3v}$ (stag) | $a_1{}^1e_1{}^1$ | $\Delta E = -4.2$ | | $e_{1/2}{}^1a_{3/2}{}^1$ | $\Delta E = +0.7$ |
| $D_{2d}$ (stag) | $a_1{}^1b_2{}^1$ | $\Delta E = -12.8$ | | $e_{1/2}{}^1e_{3/2}{}^1$ | $\Delta E = +4.5$ |
| $T_d$ (stag) | $t_2{}^2$ | $\Delta E = +38.8$ | | $u_{3/2}{}^2$ | $\Delta E = +20.9$ |
| $T_d$ (stag) | $a_1{}^1t_1{}^1$ | $\Delta E = +80.2$ | | | |
| $T_d$ (stag) | $t_2{}^1$ $t_1{}^1$ | $\Delta E = +102.1$ | | | |

verged to a slightly elongated pyramidal structure with the electron configuration $a_1{}^1e^1$.[44] The energy was 4.2 kJ $mol^{-1}$ below that calculated for the $T_d$ structure and 8.6 kJ $mol^{-1}$ above that for the $D_{2d}$ structure. Examination of the optimal $C_{3v}$ structure showed that the deformations from $T_d$ symmetry were even smaller than those of the $D_{2d}$ model described above: no valence angle changed by more than 0.2°. Single point calculations including spin−orbit coupling on the optimized $C_{3v}$ structure indicated that the most stable electron configuration is $e_{1/2}{}^1a_{3/2}{}^1$ (where $e_{1/2}$ and $a_{3/2}$ refer to the irreducible representations of the group $C_{3v}$*) and that the energy of the $C_{3v}$ structure is 0.7 kJ $mol^{-1}$ above that of the $T_d$ structure. The present calculations are hardly conclusive, but taken together the results summarized in Table 5 indicate that that Jahn−Teller distortion of the $T_d$ model is either quenched by spin−orbit coupling or very small. In this context it may be pertinent to recall that recent, careful investigations of $UCl_4$ and $UF_4$ by gas electron diffraction failed to reveal any evidence for Jahn−Teller distortion.[45,46]

When the molecular structure of $U(BH_4)_4$ was refined to the GED data under *T* symmetry, the dihedral angle $\tau(BUBH_b)$ oscillated around 60°, while the refinements failed to converge. Refinements under $T_d$ symmetry (i.e. with $\tau(BUBH_b)$ fixed at 60°) proceeded without difficulty and yielded the parameter values listed in Table 4. A series of refinements with $\tau(BUBH_b)$ fixed at values ranging from 60 to 26° in steps of 2° showed that the best fit is indeed obtained with $\tau(BUBH_b) = 60°$ and that the *R*-factor increases slowly, but monotonically, with increasing deviation from the $T_d$ model. Only when $\tau(BUBH_b)$ had been reduced to 42°, however, had the *R*-factor increased sufficiently to allow the model to be rejected at the 99.5% confidence level.[34] The GED data are clearly not good enough to allow the precise determination of H atom positions in the presence of the strongly scattering U atom.

**Vibrational Spectroscopy.** The IR spectra of matrix-isolated $Zr(BH_4)_4$ and $U(BH_4)_4$ are shown in Figure 6. Where comparisons can be made, they are consistent with the results of previous studies.[9,10,15,16,18] The spectra confirm that the equilibrium structure of each molecule is characterized by four tridentate tetrahydroborate groups. Hence we note that both display the pattern characteristic of tridentate $BH_4$ groups with but a single absorption at 2560−2600 $cm^{-1}$ corresponding to a $\nu(B-H_t)$ fundamental, a prominent doublet at 2155−2185/2090−2117 $cm^{-1}$ corresponding to $\nu(B-H_t)$ fundamentals, and a single strong absorption near 1230 $cm^{-1}$ associated with a $M(\mu\text{-}H)_3B$ deformation mode.[4,47] The case for tridentate binding is reinforced, moreover, by the resemblance, in both wavenumbers and intensities, that the spectra bear to those of such structurally authenticated tetrahydroborates as $Hf(BH_4)_4$ and $Ti(BH_4)_3$.[7,37,48] The absence of features characteristic of bidentate binding, as exhibited for instance by $Al(BH_4)_3$,[49] gives us good grounds for concluding that all the tetrahydroborate groups are indeed triply bridging, as indicated by the DFT calculations.

The high symmetry of the $M(BH_4)_4$ molecules gives rise to many degenerate normal modes; whether the molecular symmetry is *T* or $T_d$, the 57 vibrational degrees of freedom form only 24 distinct vibrational fundamentals. These span the following representations:

$T_d$ symmetry,$4a_1$ (Raman) + $1a_2$ (inactive) + 5e(Raman) + $5t_1$ (inactive) + $9t_2$ (Raman, IR);

*T* symmetry, 5a(Raman) + 5e(Raman) + 14t(Raman,IR).

Whereas $T_d$ symmetry requires only nine IR-active fundamentals in all, *T* symmetry requires fourteen, the previously silent $t_1$ modes becoming IR-active under the lower symmetry. The structural difference is, however, a small one, and the new t modes are unlikely to absorb very strongly; indeed the intensities calculated for the *T* equilibrium structure of $Zr(BH_4)_4$ indicate that the intensities of the former $t_1$ modes are less than 1% of those of the analogous former $t_2$ modes. Since the former $t_1$ and $t_2$ versions of a particular motion occur at very similar wavenumbers, there is ample opportunity for the former to be masked by the latter.

Even if the spectrum should prove to contain more lines than predicted for the $T_d$ model, these cannot be taken as a proof of symmetry lowering since they might equally well be due to $^{10}B/^{11}B$ isotopic splitting or to splitting by matrix site effects.[50,51] Additional absorptions may also be due to

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(44) A $C_{3v}$ structure with the electron configuration $a_1{}^1e^1$ is also orbitally degenerate and might suffer further J−T distortion to $C_s$ or $C_1$,[41] but these distortions were not explored.

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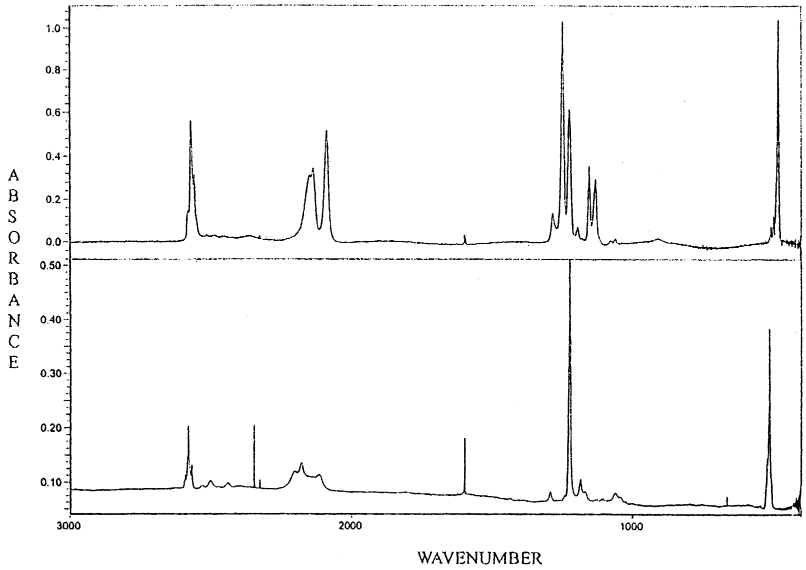

**Figure 6.** IR spectrum in the region 400−3000 cm$^{-1}$ of $U(BH_4)_4$ (above) and $Zr(BH_4)_4$ (below) each isolated in an $N_2$ matrix at 14 K.

overtone or combination bands, particularly in the critical regions associated with the $\nu$(B−H) (2000−2600 cm$^{-1}$) and the $\delta(BH_2)$ and $\nu(M-H_b)$ modes (1000−1300 cm$^{-1}$). For example, weak bands at 2504 and 2442 cm$^{-1}$ in the spectrum of matrix-isolated $Zr(BH_4)_4$ must be associated not with $\nu$(B−H) fundamentals, but with a combination and overtone, respectively, of the $\delta(BH_2)$ fundamentals occurring near 1200 cm$^{-1}$. By intensifying features such as these, Fermi resonance with neighboring fundamentals spanning the same irreducible representation may tend to blur the distinction between primary and binary transitions. Finally, possible dynamic or static Jahn−Teller distortions of $U(BH_4)_4$ represent another source of uncertainty[52,53] and spin−orbit coupling may lead to composite rather than simple vibrational wave functions. If J−T distortions and spin−orbit coupling are of comparable importance, the so-called Ham effect[53] will be operative, with significant, but largely incalculable, implications for intensity mixing of spectroscopic transitions.

In conclusion, even though other investigators have found evidence for $T$ rather than $T_d$ symmetry in the IR and Raman spectra of $Zr(BH_4)_4$,[10] we do not believe it possible to make a distinction on the basis of vibrational spectroscopy alone.

The spectra of $U(BH_4)_4$ can be satisfactorily interpreted on the basis of a $T_d$ model. Thus there are just three absorptions in the region 2000−2600 cm$^{-1}$ associated with $\nu(B-H_t)$ and $\nu(B-H_b)$ modes. The region 1000−1300 cm$^{-1}$, where $\delta(BH_2)$ and $\nu(M-H_b)$ modes occur, is made difficult to interpret by matrix and/or $^{10}B/^{11}B$ splittings, as well as problems of Fermi resonance. With the help of the spectrum calculated for the $T_d$ model, however, three features (near 1240, 1150, and 1070 cm$^{-1}$) can be identified with the $t_2$ fundamentals expected to absorb in this region. The only other strong absorption characterizing the matrix-isolated $U(BH_4)_4$ molecule, which occurs near 481 cm$^{-1}$, is readily ascribed to the $t_2$ $\nu$(U−B) mode. Of the nine IR-active fundamentals of the $U(BH_4)_4$ molecule with $T_d$ symmetry seven have thus been located more or less certainly; a $U(\mu\text{-}H)_3B$ deformation mode expected near 650 cm$^{-1}$ was evidently too weak to be observed, and a skeletal deformation mode would fall at wavenumbers below the observed range. The spectrum is thus consistent with, but does not by itself prove, $T_d$ symmetry for the equilibrium structure of $U(BH_4)_4$.

## Conclusions

Our studies of metal tetrakis(tetrahydroborate) molecules, $M(BH_4)_4$, by DFT calculations, gas electron diffraction, and matrix-isolation IR spectroscopy lead to the following conclusions.

1. Both DFT calculations and GED structure refinements indicate that the equilibrium conformation of $Zr(BH_4)_4$ has $T$ symmetry with the triply bridging $BH_4$ groups twisted about 15° away from staggered orientations. It is suggested that the small potential energy maximum at the staggered $T_d$ conformation is due to repulsion between bridging H atoms in different tetrahydroborate groups, while the much higher barrier at the eclipsed $T_d$ conformation is due to both inherent electronic effects and repulsion between bridging H atoms.

2. DFT calculations on $Hf(BH_4)_4$ indicate that the equilibrium structure is very similar to that of the Zr analogue. It is suggested that the $T_d$ molecular structure found in the solid phase is induced by intermolecular forces.

3. DFT calculations on $U(BH_4)_4$ indicate that all tetrahydroborate groups are bonded to the metal atom through triple H bridges and that the $UB_4$ coordination geometry is tetrahedral. The tridentate binding mode of the $BH_4$ groups is confirmed by matrix-isolation IR spectroscopy. Structure optimization with one of the two nonbonding 5f electrons occupying an $a_1$ and the other distributed equally over the

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three t$_2$ orbitals indicates that the equilibrium conformation has staggered BH$_4$ groups and $T_d$ symmetry. Calculations on models distorted from $T_d$ to $D_{2d}$ or $C_{3v}$ symmetry indicate that Jahn−Teller distortions are either very small or quenched by spin−orbit coupling. GED structure refinements give bond distances and valence angles in reasonable agreement with those calculated. The GED data are not good enough to allow the precise determination of H atom positions in the presence of the heavy metal atom, but the best fit between observed and calculated GED data is indeed obtained with a molecular model of $T_d$ symmetry, as indicated by the calculations.

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