

Articles

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Syntheses and Crystal Structures of the Tetrakis(methyltrihydroborato) Compounds of Zirconium(IV), Thorium(IV), Uranium(IV), and Neptunium(IV)

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Zr(BH₃CH₃)₄, Th(BH₃CH₃)₄, U(BH₃CH₃)₄, and Np(BH₃CH₃)₄ have been synthesized and their molecular structures determined by single-crystal X-ray diffraction. Infrared spectroscopy and nuclear magnetic resonance data are presented for the Zr, Th, and U compounds. The space groups, unit cell parameters, and *R* factors are as follows: Zr(BH₃CH₃)₄, tetragonal, *P*4₂/*n*, *a* = 10.311 (6) Å, *c* = 5.851 (3) Å, *Z* = 2, *d*_x = 1.103 g/cm³, *R* = 0.013 (*F*² > 3σ(*F*²)); Th(BH₃CH₃)₄, triclinic, *P*1, *a* = 18.408 (6) Å, *b* = 16.910 (6) Å, *c* = 8.834 (3) Å, α = 88.06 (4)°, β = 90.83 (4)°, γ = 88.08 (4)°, *Z* = 8, *d*_x = 1.681 g/cm³, *R* = 0.068 (*F*² > 3σ(*F*²)); U(BH₃CH₃)₄, monoclinic, *P*2₁/*n*, *a* = 18.228 (6) Å, *b* = 16.749 (6) Å, *c* = 8.765 (2) Å, β = 90.69 (4)°, *Z* = 8, *d*_x = 1.755 g/cm³, *R* = 0.041 (*F*² > 3σ(*F*²)); Np(BH₃CH₃)₄, tetragonal, *P*4₂/*n*, *a* = 10.552 (6) Å, *c* = 5.950 (3) Å, *Z* = 2, *d*_x = 1.767 g/cm³, *R* = 0.016 (*F*² > 3σ(*F*²)). All compounds are monomolecular in the crystalline state. The metal atoms are tetrahedrally coordinated to the four BH₃CH₃ groups through tridentate hydrogen bridges. The M-B distances are 2.335 ± 0.003 Å for Zr, 2.56 ± 0.05 Å for Th, 2.49 ± 0.02 Å for U, and 2.487 ± 0.006 Å for Np.

Introduction

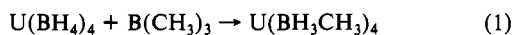
Actinide(IV) borohydrides exhibit two structural types.^{1,2} Compounds of the first type, M(BH₄)₄, where M = Th, Pa, U, are crystallographically isomorphous and are polymeric solids at room temperature with markedly different volatilities, i.e. U(BH₄)₄ readily sublimes under vacuum at 25 °C vs. ~150 °C for Th(BH₄)₄.³ Compounds of the second type are the Np and Pu borohydrides, which are volatile, chemically unstable liquids at room temperature and monomeric solids at ~10 °C.⁴ In the second type the local symmetry about the metal ion is tetrahedral and is like that found in the Zr and Hf borohydrides; however, the Np and Pu compounds crystallize in a different space group than the Zr and Hf compounds.

Schlesinger et al. have reported the synthesis and isolation of two methyl derivatives of uranium borohydride, the mono- and tetrakis(methylborohydride) derivatives, U(BH₄)₃(BH₃CH₃) and U(BH₃CH₃)₄.⁵ The mono(methylborohydride) derivative is more volatile than U(BH₄)₄ while the tetrakis(methylborohydride) derivative is slightly less volatile.

As monomeric compounds are useful for spectroscopic and magnetic measurements, we have prepared and investigated the properties of some methylated borohydrides and report in this paper the synthesis and crystal structures of M(BH₃CH₃)₄, M = Zr, Th, U, and Np.

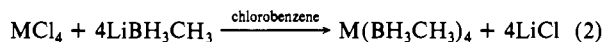
Experimental Section

U(BH₃CH₃)₄ was originally synthesized⁵ by the reaction of U(BH₄)₄ with excess trimethylboron:



This reaction also produces U(BH₃CH₃)_{*x*}(BH₄)_{4-*x*} as products, but excess trimethylboron drives the reaction to U(BH₃CH₃)₄. Our attempts with the above synthesis resulted in a low yield and substantial unreacted starting materials.

The following synthesis gave satisfactory yields:



The reaction described by eq 2 was also carried out in ether and THF. These solvents were satisfactory for Zr(BH₃CH₃)₄, but for U(BH₃CH₃)₄ and Th(BH₃CH₃)₄, adducts with the solvent were formed. Pure U(BH₃CH₃)₄ prepared in ether could be sublimed from its adduct, but Th(BH₃CH₃)₄ could not be sublimed adduct-free. Use of chlorobenzene as a solvent eliminates this problem. Np(BH₃CH₃)₄ was prepared only in chlorobenzene.

All preparations were carried out under an atmosphere of argon or under high vacuum. Chlorobenzene was dried over CaH₂ and distilled under argon before use. Melting points were determined in sealed argon-filled capillaries. ZrCl₄ was sublimed under vacuum at 300 °C for several days. UCl₄ and ThCl₄ were dried with SOCl₂ before use.

Infrared spectra were recorded on a Perkin-Elmer IR-283 spectrophotometer and calibrated with polystyrene film. Nujol and fluorolube mulls were prepared in an argon-filled drybox with dry, degassed Nujol and fluorolube. Proton magnetic resonance spectra were recorded on a Jeol FX 90Q 90-MHz FT spectrometer and referenced to Me₄Si. Samples were prepared in toluene-*d*₈ in an argon-filled drybox and sealed under vacuum. Reported values are at 25 °C.

Lithium Methyltrihydroborate. LiBH₃CH₃ was prepared according to the procedure of Wartik and Schlesinger.⁶ B(CH₃)₃ was prepared by modifying the procedure for the synthesis of B(CH₂CH₃)₃.⁷ In ~40 mL of dry mineral oil, 7.2 g (0.10 mol) of Al(CH₃)₃ was dissolved. A 3.4-g quantity (0.033 mol) of B(OCH₃)₃ was condensed onto the Al(CH₃)₃ with a -196 °C trap. The mixture was opened to a closed volume of ~1 L and slowly warmed to room temperature

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Table I. Summary of Crystal Data Intensity Collection and Least-Squares Refinement Statistics

	Zr(BH ₃ CH ₃) ₄	Np(BH ₃ CH ₃) ₄	U(BH ₃ CH ₃) ₄	Th(BH ₃ CH ₃) ₄
fw	206.7	352.5	353.5	347.5
<i>a</i> , Å	10.311 (6)	10.552 (6)	18.228 (6)	18.408 (6)
<i>b</i> , Å	10.311 (6)	10.552 (6)	16.749 (6)	16.910 (6)
<i>c</i> , Å	5.851 (3)	5.950 (3)	8.765 (2)	8.834 (3)
α, deg				88.06 (4)
β, deg			90.69 (4)	90.83 (4)
γ, deg				88.08 (4)
space group	tetragonal <i>P</i> 4 ₂ / <i>n</i>	tetragonal <i>P</i> 4 ₂ / <i>n</i>	monoclinic <i>P</i> 2 ₁ / <i>n</i>	triclinic <i>P</i> $\bar{1}$
<i>Z</i>	2	2	8	8
<i>d</i> (calcd), g/cm ³	1.103	1.767	1.755	1.681
color	colorless	dark green	violet	colorless
cryst size, mm	0.07 × 0.10 × 0.33	0.26 × 0.35 × 0.36	0.08 × 0.15 × 0.17	0.12 × 0.20 × 0.50
μ, cm ⁻¹	8	50	114	112
<i>T</i> , °C	23	23	22	22
X-ray, Mo Kα ₁ , λ, Å	0.709 30	0.709 30	0.709 30	0.709 30
2θ range, deg	4–50	4–50	4–45	4–45
no. of scans (including stds)	2623	2414	7354	12 200
decay cor range	1.00–1.03	1.00–1.04	1.00–1.14	1.00–1.28
abs cor range	1.06–1.08 ^a	2.74–5.44	2.3–4.6	2.34–5.31
no. of unique data	553	594	3295	7214
no. of data with <i>F</i> ² > 3σ used in least squares	341	345	1487	2937
ignorance factor, <i>p</i> , in weighting expression <i>w</i> = [(σ(<i>F</i> ²)) ² + (<i>pF</i> ²) ²] ⁻¹	0.02	0.015	0.05	0.05
no. of variables in least squares	45	41	163	165
<i>R</i> _w = [Σ <i>w</i> (Δ <i>F</i>) ² /Σ <i>wF</i> _o ²]	0.016	0.013	0.044	0.097
<i>R</i> = Σ Δ <i>F</i> /Σ <i>F</i> _o (<i>F</i> ² > 3σ)	0.013	0.016	0.041	0.068
<i>R</i> for all data	0.044	0.050	0.125	0.167
goodness of fit	1.03	1.00	1.06	2.61
convergence, last Δ/σ of the parameters	<0.02	<0.06	<0.02	<0.02

^a No absorption correction made.

with stirring. The B(CH₃)₃ evolved was pumped off into a -196 °C trap. This procedure was repeated twice for a total addition of 10.3 g (0.10 mol) of B(OCH₃)₃. After complete addition of B(OCH₃)₃, the crude B(CH₃)₃ collected was purified by passing it through a -132 °C trap into a -196 °C trap. A yield of 2.1 g (38%) of pure B(CH₃)₃ was obtained.

Tetrakis(methyltrihydroborato)zirconium(IV). To 0.29 g (8.1 mmol) of LiBH₃CH₃ were added 0.47 g (2.0 mmol) of ZrCl₄ and 15 mL of chlorobenzene. The mixture was stirred at ~40 °C for 48 h under argon and the solvent removed in vacuo to near dryness. Zr(BH₃CH₃)₄ was sublimed with pumping at 50 °C into a 0 °C trap for 12 h. A yield of 0.28 g (68%) of colorless crystals of Zr(BH₃CH₃)₄ that melt at 90–92 °C was recovered. Anal. Calcd for C₄H₂₄B₄Zr: C, 23.24; H, 11.70. Found: C, 23.36; H, 11.59.

Tetrakis(methyltrihydroborato)uranium(IV). To 0.30 g (8.4 mmol) of LiBH₃CH₃ were added 0.80 g (2.1 mmol) of UCl₄ and 20 mL of chlorobenzene. The mixture was stirred for 2 days under argon and then the solvent removed in vacuo to near dryness. U(BH₃CH₃)₄ was sublimed with pumping at 50 °C into a 0 °C trap over a 12-h period. A yield of 0.41 g (55%) of violet crystals of U(BH₃CH₃)₄ that melt at 72–74 °C was obtained. Anal. Calcd for C₄H₂₄B₄U: C, 13.59; H, 6.84. Found: C, 13.93; H, 7.08.

Tetrakis(methyltrihydroborato)thorium(IV). To 0.50 g (14.0 mmol) of LiBH₃CH₃ were added 1.31 g (3.5 mmol) of ThCl₄ and 20 mL of chlorobenzene. The mixture was stirred at ~40 °C for 48 h under argon and the solvent removed in vacuo to near dryness. Th(BH₃CH₃)₄ was sublimed with pumping at 50 °C into a 0 °C trap for 12 h. A yield of 0.84 g (69%) of colorless crystals of Th(BH₃CH₃)₄ that melt at 62–63 °C was recovered. Anal. Calcd for C₄H₂₄B₄Th: C, 13.83; H, 6.96. Found: C, 13.90; H, 6.85.

Tetrakis(methyltrihydroborato)neptunium(IV). To 50 mg (1.4 mmol) of LiBH₃CH₃ were added 135 mg (0.351 mmol) of NpCl₄ and 20 mL of chlorobenzene. The mixture was stirred for 15 h under argon and the solvent removed in vacuo to dryness. Np(BH₃CH₃)₄ was sublimed with pumping at room temperature into a -196 °C trap for 12 h. A yield of 10 mg (8%) of dark green crystals of Np(BH₃CH₃)₄ was obtained. Because of the low yield and the radioactivity of the product, no elemental analysis was performed.

X-ray Diffraction. All the crystals were sealed inside quartz capillaries to protect them from the atmosphere. The crystals were

examined with a Picker automated diffractometer equipped with a graphite monochromator and a Mo X-ray tube. In each structure determination, the setting angles of several centered reflections were used for the least-squares adjustment of the cell dimensions; cell dimensions and other crystal data are given in Table I.

For the Zr and U compounds a θ - 2θ scan technique with a fixed scan speed of 2°/min was used to collect the intensities. Backgrounds were measured for 10 s (Zr) and 4 s (U) at the beginning and end of each scan. For the Th compound a θ - 2θ scan technique was used with a variable scan rate that ranged from 2 to 8°/min on 2θ ; a scan consists of 76 steps across (1.5 + 0.693 tan θ)° of 2θ for the peak and an additional 12 steps on each side of the peak scan for the background. The reflection was first scanned at 8°/min (2θ) and was accepted as measured if the estimated standard deviation was less than 2% of the net count or the net count was less than its estimated standard deviation; otherwise, a second scan was performed at either a speed that would yield 2% accuracy or a speed of 2°/min, and the results of the second scan were added to the first. For the Np compound, the data was collected by ω scans rather than θ - 2θ scans because the reflections in the Np compound were very broad in ω , i.e. ω peak widths at half-height ranged from 0.3 to 1°. Each peak scan consisted of 76 steps across (2.25 + 0.346 tan θ)° in ω , centered at zero ω , and an additional 12 steps on each side of the peak scan for the background. The remaining details of data collection are similar to those for the Th compound data collection.

Standard reflections were measured after 250 scans, and these variations were used to adjust the data. Lorentz and polarization corrections were applied, and absorption corrections were made, for all but the Zr compound, with use of an analytical integration method.⁸

The structures were refined by a full-matrix least-squares procedure in which the function $\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$ was minimized. Atomic scattering factors for all atoms except hydrogen were taken from ref 9; the hydrogen scattering factors were those of Stewart, Davidson, and Simpson.¹⁰ Anomalous scattering corrections of

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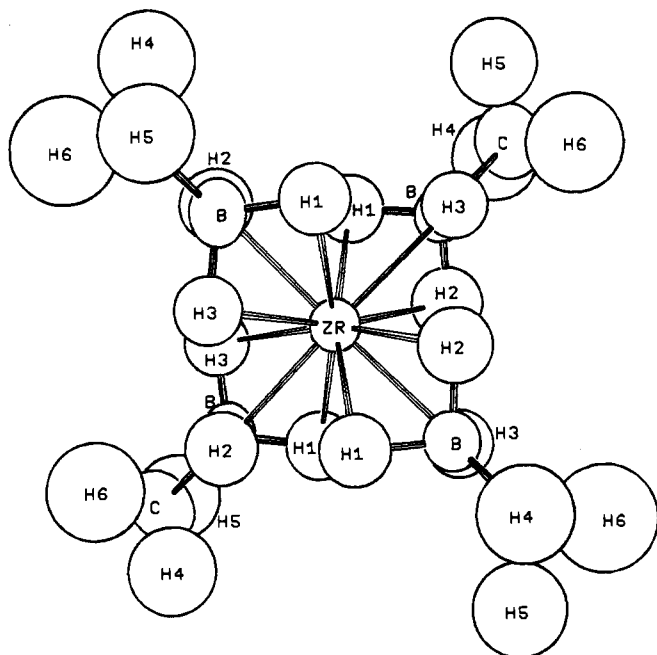


Figure 1. ORTEP drawing of Zr(BH₃CH₃)₄.

Cromer and Liberman¹¹ were applied.

Determination of Structures. For the Zr and U structures three-dimensional Patterson maps were used to find the metal atoms, and subsequent least-squares refinements and electron density maps were used to find the remaining atoms. The least-squares refinements of the Np and Th structures were started with the atomic positions found in the Zr and U structures, respectively. Hydrogen atoms were found and refined in the Zr structure; they were included in the Np structure, but in a restrained fashion. The metal atoms were all refined anisotropically; the B and C atoms were refined anisotropically in all the structures with the exception of the Th compound, where the attempt to refine these atoms anisotropically gave non-positive-definite thermal parameters. *R* factors and other statistical results of the least-squares refinements are given in Table I.

Positional parameters are given in Table II, and distances and angles are given in Tables III and IV. Tables of thermal parameters, observed structure factors, and calculated powder patterns are given as supplementary material.

Results and Discussion

Zr(BH₃CH₃)₄, Np(BH₃CH₃)₄, Th(BH₃CH₃)₄, and U(BH₃CH₃)₄ are monomolecular in the crystalline state. The metal atom is tetrahedrally coordinated to the four methylborohydride groups of the molecule. Twelve hydrogen atoms from the BH₃ entities are in close contact to the metal atom (see Figure 1). With the exception of the methyl groups, the molecular geometry of Zr(CH₃BH₃)₄ is the same as that suggested for Zr(BH₄)₄ at -160 °C¹² and found for Np(BH₄)₄ at -143 °C.²

The Zr(BH₃CH₃)₄ and Np(BH₃CH₃)₄ structures consist of a body-centered packing of molecules (Figure 2). The coordination in these two compounds is similar to that found in their borohydrides.² The Zr-B distances in Zr(BH₃CH₃)₄ and Zr(BH₄)₄ are 2.335 (3) and 2.34 (3) Å, respectively;¹² the Np-B distances in Np(BH₃CH₃)₄ and Np(BH₄)₄ are 2.487 (6) and 2.46 (3) Å, respectively.²

The Th and U complexes are very near to being crystallographically isomorphous. The uranium compound is in a monoclinic space group, but in the Th compound the *b* axis is inclined to the *ac* plane by about 2°, which results in a

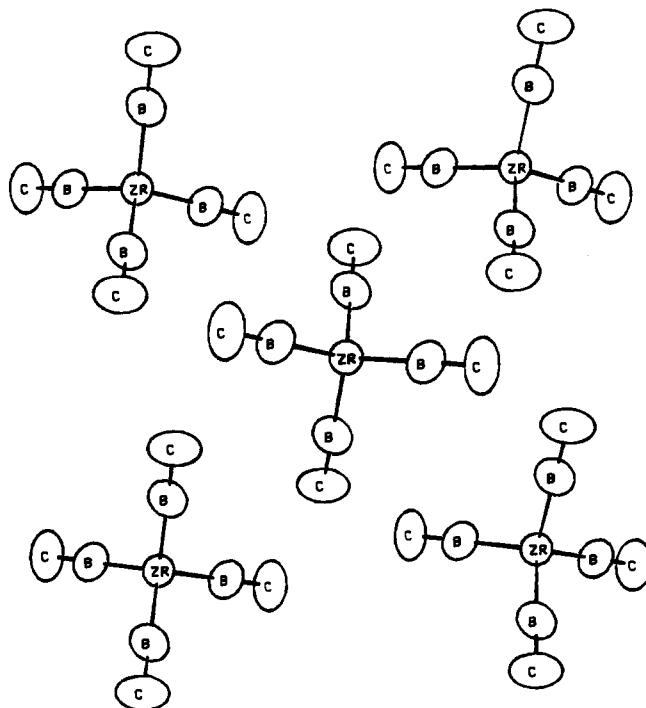


Figure 2. ORTEP drawing showing packing of Zr(BH₃CH₃)₄ units. The central molecule is displaced by $\frac{1}{2}a$, $\frac{1}{2}b$, $\frac{1}{2}c$ from the corner molecules.

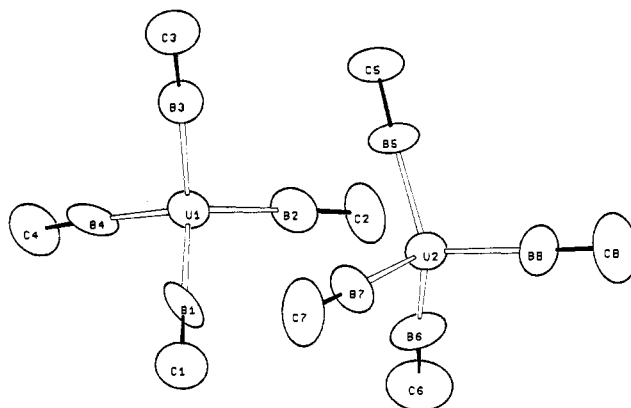


Figure 3. ORTEP drawing of the U(BH₃CH₃)₄ structure.

triclinic space group. Whereas in the uranium compound the unit cell contains two crystallographically different but chemically identical molecules, the thorium compound contains four. Within these structures the M-B bond lengths deviate less than 2σ (for U) and 3σ (for Th) from their respective average, and the B-M-B angles in both structures are all within 3σ of being tetrahedral.

The average triple-hydrogen-bridged U-B distance in U(BH₃CH₃)₄ is 2.48 ± 0.03 Å. These may be compared to triply bridged distances found in U(BH₄)₄⁶ (2.52 (1) Å), U(BH₄)₄·O(C₂H₅)₂¹³ (2.53 (2) Å), and U(BH₄)₄·2OC₄H₈¹⁴ (2.56 (4) Å). These last three compounds are all 14-coordinate, and thus we would expect the U(IV) ionic radius and consequently the U-B distance to be slightly greater for these compounds than for 12-coordinate U(BH₃CH₃)₄.¹⁵

The B-C distances in the Zr and Np complexes are ~0.08 Å shorter than in the U and Th complexes. We believe this difference is the result of not including the hydrogen atoms

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Table II. Positional Parameters

atom	x	y	z
Zr(BH ₃ CH ₃) ₄			
Zr	0.250	0.250	0.250
B	0.2844 (3)	0.4318 (3)	0.4801 (6)
C	0.3077 (5)	0.5544 (4)	0.6347 (10)
H(1)	0.2828 (25)	0.4484 (25)	0.286 (5)
H(2)	0.1892 (27)	0.3799 (27)	0.489 (5)
H(3)	0.3535 (25)	0.3449 (25)	0.503 (5)
H(4)	0.251 (5)	0.611 (5)	0.611 (7)
H(5)	0.389 (4)	0.605 (4)	0.605 (7)
H(6)	0.317 (6)	0.537 (5)	0.776 (9)
U(BH ₃ CH ₃) ₄			
U(1)	0.37224 (5)	0.17396 (5)	0.03540 (10)
U(2)	0.29978 (5)	0.50614 (6)	-0.02715 (10)
B(1)	0.2398 (14)	0.2053 (14)	0.074 (4)
B(2)	0.4495 (18)	0.2726 (19)	0.169 (4)
B(3)	0.4024 (19)	0.1805 (18)	-0.241 (3)
B(4)	0.3945 (16)	0.0356 (19)	0.131 (4)
B(5)	0.4049 (16)	0.4451 (18)	-0.1668 (27)
B(6)	0.3070 (17)	0.4687 (19)	0.241 (3)
B(7)	0.1790 (16)	0.4588 (16)	-0.132 (4)
B(8)	0.3037 (20)	0.6507 (17)	-0.045 (4)
C(1)	0.1524 (14)	0.2278 (16)	0.092 (3)
C(2)	0.5002 (16)	0.3388 (16)	0.264 (3)
C(3)	0.4229 (16)	0.1803 (17)	-0.4169 (28)
C(4)	0.4092 (15)	-0.0503 (14)	0.205 (4)
C(5)	0.4755 (14)	0.4084 (16)	-0.253 (3)
C(6)	0.3154 (19)	0.4505 (20)	0.428 (3)
C(7)	0.1013 (15)	0.4267 (15)	-0.203 (3)
C(8)	0.3026 (18)	0.7513 (15)	-0.072 (4)
Np(BH ₃ CH ₃) ₄			
Np	0.250	0.250	0.250
B	0.2873 (6)	0.4390 (5)	0.4906 (9)
C	0.3077 (8)	0.5590 (6)	0.6403 (11)
H(1)	0.308 (5)	0.448 (5)	0.319 (4)
H(2)	0.2025 (23)	0.386 (4)	0.506 (7)
H(3)	0.350 (4)	0.357 (3)	0.506 (8)
H(4)	0.264 (5)	0.634 (4)	0.595 (9)
H(5)	0.3909 (29)	0.592 (6)	0.610 (11)
H(6)	0.300 (7)	0.551 (7)	0.798 (3)
Th(BH ₃ CH ₃) ₄			
Th(1)	0.37160 (11)	0.17353 (10)	0.02097 (21)
Th(2)	0.12319 (11)	0.67806 (10)	0.45297 (21)
Th(3)	0.29973 (11)	0.50803 (11)	-0.03111 (21)
Th(4)	0.19932 (10)	0.00358 (10)	0.51394 (19)
B(1)	0.237 (3)	0.208 (3)	0.069 (7)
B(2)	0.453 (4)	0.271 (4)	0.147 (8)
B(3)	0.399 (3)	0.1835 (28)	-0.263 (6)
B(4)	0.394 (3)	0.032 (3)	0.103 (7)
B(5)	0.259 (3)	0.7069 (28)	0.429 (6)
B(6)	0.054 (3)	0.787 (3)	0.313 (7)
B(7)	0.092 (4)	0.679 (4)	0.728 (9)
B(8)	0.104 (3)	0.5403 (29)	0.363 (6)
B(9)	0.410 (3)	0.449 (3)	-0.166 (7)
B(10)	0.313 (4)	0.461 (4)	0.246 (8)
B(11)	0.177 (4)	0.452 (4)	-0.158 (8)
B(12)	0.305 (4)	0.660 (4)	-0.058 (7)
B(13)	0.092 (3)	0.937 (3)	0.655 (7)
B(14)	0.194 (3)	0.977 (3)	0.239 (7)
B(15)	0.323 (3)	0.953 (3)	0.621 (7)
B(16)	0.188 (3)	1.154 (3)	0.543 (7)
C(1)	0.147 (4)	0.241 (4)	0.097 (7)
C(2)	0.503 (3)	0.3309 (29)	0.231 (6)
C(3)	0.4083 (27)	0.1919 (25)	-0.460 (6)
C(4)	0.4103 (28)	-0.0600 (27)	0.189 (6)
C(5)	0.344 (3)	0.7299 (29)	0.409 (6)
C(6)	-0.0015 (24)	0.8500 (23)	0.205 (5)
C(7)	0.0653 (28)	0.6740 (27)	0.893 (6)
C(8)	0.0941 (23)	0.4510 (22)	0.300 (5)
C(9)	0.482 (3)	0.4101 (28)	-0.249 (6)
C(10)	0.315 (3)	0.435 (3)	0.428 (7)
C(11)	0.1006 (27)	0.4297 (25)	-0.217 (5)
C(12)	0.295 (3)	0.752 (3)	-0.064 (7)
C(13)	0.0262 (27)	0.9038 (26)	0.756 (6)
C(14)	0.179 (3)	0.958 (3)	0.059 (7)
C(15)	0.4036 (28)	0.9193 (27)	0.672 (6)
C(16)	0.1837 (28)	1.2490 (27)	0.561 (6)

Table III. Selected Interatomic Distances (Å)

	Zr(BH ₃ CH ₃) ₄	Np(BH ₃ CH ₃) ₄		
M-B	2.335 (3)	2.487 (6)		
-4H(1)	2.08 (3)	2.22 ^a		
-4H(2)	2.04 (3)	2.15		
-4H(3)	2.07 (3)	2.16		
B-C	1.573 (5)	1.563 (8)		
-H(1)	1.15 (3)	1.05		
-H(2)	1.12 (3)	1.06		
-H(3)	1.15 (3)	1.09		
C-H(4)	0.84 (5)	0.96		
-H(5)	1.00 (4)	0.96		
-H(6)	0.85 (5)	0.94		
U(BH ₃ CH ₃) ₄				
U(1)-B(1)	2.50 (4)	U(2)-B(5)	2.50 (3)	
-B(2)	2.46 (4)	-B(6)	2.44 (4)	
-B(3)	2.49 (4)	-B(7)	2.50 (3)	
-B(4)	2.50 (4)	-B(8)	2.43 (3)	
B(1)-C(1)	1.65 (4)	B(5)-C(5)	1.62 (4)	
B(2)-C(2)	1.66 (4)	B(6)-C(6)	1.67 (4)	
B(3)-C(3)	1.59 (4)	B(7)-C(7)	1.63 (4)	
B(4)-C(4)	1.60 (4)	B(8)-C(8)	1.70 (4)	
Th(BH ₃ CH ₃) ₄				
Th(1)-B(1)	2.57 (6)	Th(3)-B(9)	2.56 (6)	
-B(2)	2.54 (7)	-B(10)	2.55 (7)	
-B(3)	2.57 (6)	-B(11)	2.71 (7)	
-B(4)	2.49 (6)	-B(12)	2.58 (6)	
Th(2)-B(5)	2.57 (6)	Th(4)-B(13)	2.61 (6)	
-B(6)	2.50 (6)	-B(14)	2.49 (6)	
-B(7)	2.51 (8)	-B(15)	2.57 (6)	
-B(8)	2.52 (5)	-B(16)	2.56 (5)	
B(1)-C(1)	1.76 (8)	B(9)-C(9)	1.65 (7)	
B(2)-C(2)	1.59 (7)	B(10)-C(10)	1.65 (8)	
B(3)-C(3)	1.76 (7)	B(11)-C(11)	1.57 (8)	
B(4)-C(4)	1.73 (7)	B(12)-C(12)	1.57 (7)	
B(5)-C(5)	1.63 (7)	B(13)-C(13)	1.63 (7)	
B(6)-C(6)	1.70 (7)	B(14)-C(14)	1.66 (8)	
B(7)-C(7)	1.55 (8)	B(15)-C(15)	1.62 (9)	
B(8)-C(8)	1.64 (6)	B(16)-C(16)	1.63 (7)	
Averages ^b				
	Zr	Th	U	Np
M-B	2.335 (3)	2.56 ± 0.05	2.48 ± 0.03	2.487 (6)
B-C	1.573 (5)	1.65 ± 0.06	1.64 ± 0.04	1.563 (8)

^a Hydrogens in Np(BH₃CH₃)₄ were refined with restrained distances. ^b There is only one type of M-B and B-C bond length in the Zr and Np compounds, and the estimated standard deviation in parentheses is that from the least-squares refinement. The estimated deviations for the U and Th distances are given as ± and are calculated as $[(\Sigma d^2 - (\Sigma d)^2/n)/(n-1)]^{1/2}$, where d is the distance and n the number of distances.

in the least-squares refinement of the U and Th complexes. When the hydrogen atoms are not included, the two light atoms tend to shift apart to compensate for electron density near the unresolved hydrogen atoms. In the early stages of the refinement of the Zr structure the B-C distance was 1.61 Å before the hydrogen atoms were included. The above argument would also suggest the U-B and Th-B distances would be slightly longer than shown in Table III.

The compounds were characterized by infrared and proton NMR spectroscopy. The data are presented in Tables V and VI, respectively. From the assignments of Marks et al.¹⁶ and Banks and Edelstein,¹⁷ the infrared spectrum shows the presence of B-H_b stretches at ~2100 cm⁻¹ and bridge deformation at ~1250 cm⁻¹ and the complete absence of B-H_t stretches at ~2500 cm⁻¹. The other bands listed are due to the presence of the methyl group. The ¹H NMR spectrum of Zr(BH₃CH₃)₄ shows a quartet due to the three bridging

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Table IV. Selected Angles (deg)

	M(BH ₃ CH ₃) ₄	
	M = Zr	M = Np
B-M-B ^a	109.6 (2)	109.7 (3)
B-M-B ^b	109.4 (1)	109.4 (2)
M-B-C	179.9 (3)	178.7 (5)
H(1)-B-H(2)	96 (2)	108 ^c
H(1)-B-H(3)	104 (2)	92
H(2)-B-H(3)	99 (2)	95
H(4)-C-H(5)	101 (4)	95
H(4)-C-H(6)	113 (5)	108
H(5)-C-H(6)	101 (5)	108
	U(BH ₃ CH ₃) ₄	
B(1)-U(1)-B(2)	110 (1)	B(6)-U(2)-B(8) 109 (1)
B(1)-U(1)-B(3)	110 (1)	B(7)-U(2)-B(8) 109 (1)
B(1)-U(1)-B(4)	108 (1)	U(1)-B(1)-C(1) 178 (2)
B(2)-U(1)-B(3)	108 (1)	U(1)-B(2)-C(2) 178 (2)
B(2)-U(1)-B(4)	112 (2)	U(1)-B(3)-C(3) 177 (2)
B(3)-U(1)-B(4)	109 (1)	U(1)-B(4)-C(4) 176 (3)
B(5)-U(2)-B(6)	110 (1)	U(2)-B(5)-C(5) 177 (2)
B(5)-U(2)-B(7)	111 (1)	U(2)-B(6)-C(6) 175 (3)
B(5)-U(2)-B(8)	111 (1)	U(2)-B(7)-C(7) 179 (2)
B(6)-U(2)-B(7)	108 (1)	U(2)-B(8)-C(8) 175 (3)
	Th(BH ₃ CH ₃) ₄	
B(1)-Th(1)-B(2)	110 (2)	B(13)-Th(4)-B(16) 109 (2)
B(1)-Th(1)-B(3)	111 (2)	B(14)-Th(4)-B(15) 109 (2)
B(1)-Th(1)-B(4)	107 (2)	B(14)-Th(4)-B(16) 108 (2)
B(2)-Th(1)-B(3)	106 (2)	B(15)-Th(4)-B(16) 109 (2)
B(2)-Th(1)-B(4)	115 (2)	Th(1)-B(1)-C(1) 175 (4)
B(3)-Th(1)-B(4)	107 (2)	Th(1)-B(2)-C(2) 178 (4)
B(5)-Th(2)-B(6)	107 (2)	Th(1)-B(3)-C(3) 174 (4)
B(5)-Th(2)-B(7)	108 (2)	Th(1)-B(4)-C(4) 171 (4)
B(5)-Th(2)-B(8)	108 (2)	Th(2)-B(5)-C(5) 177 (4)
B(6)-Th(2)-B(7)	110 (2)	Th(2)-B(6)-C(6) 171 (4)
B(6)-Th(2)-B(8)	116 (2)	Th(2)-B(7)-C(7) 174 (5)
B(7)-Th(2)-B(8)	107 (2)	Th(2)-B(8)-C(8) 177 (4)
B(9)-Th(3)-B(10)	106 (2)	Th(3)-B(9)-C(9) 179 (4)
B(9)-Th(3)-B(11)	109 (2)	Th(3)-B(10)-C(10) 175 (5)
B(9)-Th(3)-B(12)	108 (2)	Th(3)-B(11)-C(11) 171 (4)
B(10)-Th(3)-B(11)	111 (2)	Th(3)-B(12)-C(12) 171 (5)
B(10)-Th(3)-B(12)	111 (2)	Th(4)-B(13)-C(13) 174 (4)
B(11)-Th(3)-B(12)	112 (2)	Th(4)-B(14)-C(14) 172 (4)
B(13)-Th(4)-B(14)	111 (2)	Th(4)-B(15)-C(15) 175 (4)
B(13)-Th(4)-B(15)	112 (2)	Th(4)-B(16)-C(16) 178 (4)

^a At position 1/2 - x, 1/2 - y, z. ^b At position y, 1/2 - x, 1/2 - z.
^c Hydrogens refined in least squares with restrained distances.

Table V. Infrared Spectroscopic Data (cm⁻¹) for M(BH₃CH₃)₄ Compounds

compd	
Zr(BH ₃ CH ₃) ₄	2950 m, 2140 w, 2080 m, 1310 m, 1230 m, 1090 w, 1020 w, 1000 w, 890 w
U(BH ₃ CH ₃) ₄	2950 m, 2130 w, 2050 m, 1310 m, 1270 m, 1080 w, 1020 w, 1000 w, 910 w
Th(BH ₃ CH ₃) ₄	2950 m, 2165 w, 2070 m, 1310 m, 1260 m, 1090 w, 1015 w, 990 w, 870 w

borohydride protons with nearly the same chemical shift as that of Zr(BH₃CH₃)₄. For all compounds the spectra of the bridging protons are broadened due to quadrupole relaxation by ^{10,11}B. This effect obscures the boron-hydrogen spin-spin

Table VI. Nuclear Magnetic Resonance Data for M(BH₃CH₃)₄ Compounds^{a,b}

compd	
Zr(BH ₃ CH ₃) ₄	+0.25 ^c (12 H, s), +1.43 (12 H, quart)
U(BH ₃ CH ₃) ₄	+15.8 (12 H, s), +156.4 (12 H, quart)
Th(BH ₃ CH ₃) ₄	+0.11 (12 H, quart), +3.43 (12 H, quart)

^a All samples prepared in toluene-*d*₈. ^b Shifts in ppm from Me₄Si. Positive sign indicates a downfield shift. All values are at 25 °C. ^c Broadened due to unresolved spin-spin coupling and quadrupole relaxation with ^{10,11}B.

coupling.¹⁸ The bridging protons of U(BH₃CH₃)₄ are shifted far downfield due to the paramagnetic U(IV). The methyl proton signal for Th(BH₃CH₃)₄ at room temperature is a quartet due to the boron-hydrogen spin-spin coupling but again is broadened by the quadrupole relaxation of ^{10,11}B.

The early members of the An(BH₃CH₃)₄ series, Th, Pa, and U, exhibit a polymeric structure, whereas the later members, Np and Pu, exhibit a monomeric structure that is closely related to that for Hf and Zr borohydrides. Replacement of the BH₄⁻ group by the BH₃CH₃⁻ group results in the formation of monomeric compounds for the above actinides. Nevertheless, the crystal structure of Np(BH₃CH₃)₄ is like that of Zr(BH₃CH₃)₄ rather than of U(BH₃CH₃)₄ despite the fact that the U⁴⁺ ion is only slightly larger than Np⁴⁺ (+0.02 Å for eight-coordination) and the Zr⁴⁺ ion is considerably smaller (-0.12 Å for eight-coordination).¹⁹ Qualitatively, this difference is reflected in the volatility of the compounds, with Np(BH₃CH₃)₄ and Zr(BH₃CH₃)₄ being of comparable volatility and both being more volatile than either U(BH₃CH₃)₄ or Th(BH₃CH₃)₄. Th(BH₃CH₃)₄ sublimes easily under vacuum at ~40 °C, which makes it the most volatile compound of thorium known to date.

Spectral and magnetic studies on some of these compounds will be reported separately.

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Registry No. Zr(BH₃CH₃)₄, 86217-19-8; Th(BH₃CH₃)₄, 86238-35-9; U(BH₃CH₃)₄, 86217-20-1; Np(BH₃CH₃)₄, 86217-21-2.

Supplementary Material Available: Listings of thermal parameters, calculated powder patterns, and observed structure factors (52 pages). Ordering information is given on any current masthead page.

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