

possibility that small amounts of the other two isomers may have been formed and escaped detection, an adequate explanation of the preference for the title compound is not apparent at this time.

Acknowledgment. This work was supported by the Robert A. Welch Foundation of Houston, Tex., Grant A-614.

Registry No. $[\eta^4-C_4(C_3H_3)_2(CH_3)_2CO]Fe(CO)_3$, 65120-33-4; $[\eta^4-C_4(C_3H_3)_2(CH_3)_2CO]Fe(CO)_3$ -(previous formulation), 65120-32-3.

Supplementary Material Available: Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720

Preparation and Molecular and Crystal Structures of Uranium(IV) Borohydride-Dimethyl Ether and Uranium(IV) Borohydride-Diethyl Ether¹

RICHARD R. RIETZ, ALLAN ZALKIN,* DAVID H. TEMPLETON,* NORMAN M. EDELSTEIN,* and LIESELOTTE K. TEMPLETON

Received July 21, 1977

Uranium(IV) borohydride reacts with dimethyl ether and diethyl ether to form $U(BH_4)_4 \cdot O(CH_3)_2$ and $U(BH_4)_4 \cdot O(C_2H_5)_2$, respectively. The yields are >90%. The latter compound can also be prepared by reacting UF_4 and $LiBH_4$ in diethyl ether for 1 week. Both compounds are green, crystalline solids that can be sublimed in bulk at 50 °C and 10^{-5} mm. Single-crystal x-ray diffractometry has shown both of these materials to be monoether complexes in the solid state. $U(BH_4)_4 \cdot O(CH_3)_2$ is orthorhombic, *Pnma*, with $a = 11.423$ (5) Å, $b = 10.120$ (4) Å, $c = 9.915$ (4) Å, and $Z = 4$. $U(BH_4)_4 \cdot O(C_2H_5)_2$ is monoclinic, *P2₁*, with $a = 7.95$ (1) Å, $b = 15.24$ (1) Å, $c = 5.74$ (1) Å, $\beta = 106.0$ (1)°, and $Z = 2$. The structure of each complex consists of infinite linear chains of alternating uranium and boron atoms joined by double-hydrogen-bridge bonds. The remaining borohydrides are attached to the uranium atom by triple-hydrogen-bridge bonds. The ether moieties are associated to the uranium by the oxygen atoms. In the dimethyl ether adduct successive ether molecules along the chain are trans, whereas in the diethyl ether compound they are all cis. The total coordination about the uranium atom is 14, i.e., 1 oxygen atom and 13 hydrogen atoms. The average U-B distances for the triple-bridge and double-bridge bonds are 2.53 (2) and 2.89 (1) Å, respectively. The average U-O bond length is 2.46 (3) Å. A refinement of the anomalous dispersion term f'' for uranium in the ethyl compound shows that the crystal was twinned, containing unequal fractions of the enantiomeric configurations.

Introduction

Uranium(IV) borohydride, a volatile, dark green, crystalline compound obtained by treating UF_4 with $Al(BH_4)_3$ at room temperature, was first synthesized by Schlesinger and Brown during the Manhattan project and reported in 1953.^{2,3} In an attempt to prepare $U(BH_4)_4$ by another route, they treated UF_4 with $LiBH_4$ in the presence of ether to form a green, ether-soluble product but were unable to completely separate this material from the solvent. $U(BH_4)_4$ formed a 1:1 complex with ethyl ether which was stable at -80 °C, but pure $U(BH_4)_4$ could not be recovered by high-vacuum fractional distillation.

Recently, Russian workers⁴ have published a new synthesis of $U(BH_4)_4$ by the reaction of finely powdered UCl_4 and $LiBH_4$ (in a vacuum vibration ball mill). This synthesis parallels the well-known method for producing $Hf(BH_4)_4$ and $Zr(BH_4)_4$ ⁵ and avoids the use of $Al(BH_4)_3$, a liquid explosive to oxygen or water.

Hoekstra and Katz⁶ have reported the synthesis of the isomorphous but much less volatile actinide compound $Th(BH_4)_4$ by treating ThF_4 with $Al(BH_4)_3$. Subsequently, Ehemann and Nöth⁷ synthesized $Th(BH_4)_4$ by the reaction of $ThCl_4$ with $LiBH_4$ in diethyl ether. Here, an etherate complex was formed as an intermediate, but the solvent could be completely removed by vacuum distillation. Consistent with this synthesis

was the isolation by Hoekstra and Katz⁶ of $Th(BH_4)_4 \cdot 2(C_2H_5)_2O$ by dissolution of $Th(BH_4)_4$ in diethyl ether with partial recovery of the $Th(BH_4)_4$ after heating under vacuum. Ehemann and Nöth⁷ also treated $Th(BH_4)_4$ with $LiBH_4$ in diethyl ether and reported the synthesis of the salts $LiTh(BH_4)_5$ and $Li_2Th(BH_4)_6$. Etherates were again formed as intermediates, but the diethyl ether was easily removed.

In our search for new volatile actinide compounds, we have prepared a number of Lewis-base adducts of uranium(IV) borohydride by direct combination of $U(BH_4)_4$ and the Lewis base.⁸ Many of these materials are volatile, among them $U(BH_4)_4 \cdot O(CH_3)_2$ and $U(BH_4)_4 \cdot O(C_2H_5)_2$. We have also repeated the work of Schlesinger and Brown² and have shown their "etherate unstable at room temperature" is actually the stable compound $U(BH_4)_4 \cdot O(C_2H_5)_2$.

Experimental Section

Materials and Chemical Techniques. $U(BH_4)_4$ was prepared by the method of Schlesinger and Brown² and purified by sublimation at 30-40 °C and 10^{-5} mm. UF_4 (Alfa) was vacuum-dried at 300 °C for 3 days. Dimethyl ether (Matheson) was purified by passage through a -78 °C trap until its vapor pressure was 283 mm.⁹ Diethyl ether (Mallinckrodt) was doubly distilled from sodium/benzophenone under argon. All manipulations were performed in mercury-, oil-, and grease-free Pyrex high-vacuum lines or in argon-filled dryboxes.⁹

Preparation of $U(BH_4)_4 \cdot O(CH_3)_2$. A 250-mL flask was loaded with 0.29 g of $U(BH_4)_4$ (0.975 mmol) in a drybox. The flask was fitted with a vacuum-line adapter, sealed, removed to the vacuum line, cooled to $-196^\circ C$, and evacuated. Dimethyl ether (3.58 mmol) was condensed onto the flask walls. The vessel was warmed to room temperature. No reaction was noted between the gaseous $(CH_3)_2O$ and the solid $U(BH_4)_4$. The vessel was cooled to $-196^\circ C$ and an additional 40 mmol of $(CH_3)_2O$ was condensed in. The vessel was slowly warmed to $-78^\circ C$. No reaction was noted. When the vessel was warmed to $-30^\circ C$, the $U(BH_4)_4$ first turned white and then went into solution. Green crystals could be forced out of solution by cooling to $-78^\circ C$, but rearming to $-30^\circ C$ only produced the green solution. The white intermediate stage was only seen upon the first dissolution. This phenomenon was observed in every preparation of $U(BH_4)_4 \cdot O(CH_3)_2$ and $U(BH_4)_4 \cdot O(C_2H_5)_2$. After 30 min at $-30^\circ C$, the flask was cooled to $-78^\circ C$ and the excess $(CH_3)_2O$ was stripped off. The product was pumped at $20^\circ C$ into a tared trap at $-78^\circ C$. A 0.317-g weight of green crystals (mp $93^\circ C$, sealed capillary) was recovered. Based on the empirical formula, this is 0.924 mmol (95% yield).

$U(BH_4)_4 \cdot O(CH_3)_2$ hydrolyzes slowly in air and inflames upon contact with water. It can be sublimed in bulk at $50^\circ C$. It has been kept under argon or vacuum for several months with little decomposition. Its physical and spectroscopic properties will appear in a subsequent publication.⁸

Direct Preparation of $U(BH_4)_4 \cdot O(C_2H_5)_2$. In a typical preparation, 0.396 g of $U(BH_4)_4$ (1.33 mmol) was sublimed into a 100-mL trap. Diethyl ether (6.54 g) was condensed on top of the $U(BH_4)_4$ at $-196^\circ C$. The trap was sealed, removed from the vacuum line, and slowly warmed to room temperature with shaking. At $\sim -30^\circ C$ the $U(BH_4)_4$ turned white and then quickly dissolved to form a deep green solution. Green crystals could be obtained by cooling the solution. This phenomenon is described above. After 30 min at room temperature, the trap was cooled to $-78^\circ C$ and then reattached to the vacuum line, and the excess $(C_2H_5)_2O$ was removed by pumping for 4 h. The product was pumped at $20^\circ C$ to another tared trap at $-78^\circ C$. A 0.464-g quantity of green crystals (mp $66^\circ C$, sealed capillary) was recovered. Based on the empirical formula, this is 1.25 mmol (94% yield).

$U(BH_4)_4 \cdot O(C_2H_5)_2$ hydrolyzes slowly in air and inflames, often with an explosion, upon contact with water. It can be sublimed in bulk at $50^\circ C$. It has been kept for 6 months under vacuum or under argon without decomposition. Its physical and spectroscopic properties will appear in a subsequent publication.⁸

Preparation of $U(BH_4)_4 \cdot O(C_2H_5)_2$ from UF_4 and $LiBH_4$ in Diethyl Ether. Ten grams of finely ground UF_4 (31.85 mmol) was loaded into a 250-mL Schlenk flask containing a Teflon stirring egg. The flask was moved into the drybox where 2.8 g of finely ground $LiBH_4$ (128.6 mmol) was added. The flask was fitted with a vacuum adapter, sealed, and moved to the vacuum line. After thorough evacuation to remove trapped argon (1 h), ~ 125 mL of diethyl ether was condensed in at $-196^\circ C$. The flask was sealed, removed from the vacuum line, and warmed to room temperature with stirring (~ 1 h). The stirrer was shut off occasionally to observe the ether solution. At 2 h it was colorless as it was at 6 h. At 1 day, it was faint green. At 8 days, the solution was dark green and a gray-white precipitate had formed.

At this point, the flask was filled with argon, and the contents were Schlenk filtered under argon through a medium frit. The green filtrate was concentrated by pumping at $-78^\circ C$ under high vacuum. When the bulk of the ether had distilled off, the product was pumped at $20^\circ C$ to a tared trap at $-78^\circ C$.¹⁰ Yield: 4.45 g, 38% based on UF_4 . No attempt was made to recover the unused UF_4 . Identification of the product as $U(BH_4)_4 \cdot O(C_2H_5)_2$ was made by its melting point, infrared spectrum, and x-ray powder patterns.⁸

A nonvolatile, ether-soluble, greenish white, uranium-containing material was left after removing the $U(BH_4)_4 \cdot O(C_2H_5)_2$ from the filtrate. Absorption bands for uranium-borohydride units appeared in the infrared spectrum of this material. The compound hydrolyzed quickly in air, sometimes catching fire. It often exploded on contact with water. We believe it is a mixture of $UF_x(BH_4)_{4-x}$ species, possibly with associated ethers. No attempts were made to recycle this material.

Crystal Growth. The only method which gave crystals suitable for x-ray diffraction was as follows. Several crystals were ground in an agate mortar and pestle and poured into a capillary drawn from a 14/35 quartz joint. An adapter containing a stopcock to trap argon over the sample was placed over the loaded joint. This assembly was

Table I. Summary of Crystal Data and Intensity Collection

	$U(BH_4)_4 \cdot O(CH_3)_2$	$U(BH_4)_4 \cdot O(C_2H_5)_2$
Fw	343.47	371.52
a, Å	11.423 (5)	7.945 (10)
b, Å	10.120 (4)	15.244 (10)
c, Å	9.915 (4)	5.740 (10)
β , deg	90.0	106.04 (10)
V, Å ³	1146	668
Z	4	2
Density (calcd), g/cm ³	1.99	1.85
Space group	<i>Pnma</i>	<i>P2₁</i>
Cryst shape and size	Irregular shape; 0.10 × 0.15 × 0.30 mm	Five-sided plate of 7 faces 001, 00 $\bar{1}$, 110, 100, 140, 140, 110; 0.1 × 0.3 × 0.3 mm
Cryst vol, mm ³	0.004	0.0083
Temp, °C	23	21
Radiation	Mo K α (λ 0.709 26 and 0.713 54 Å) monochromated from (002) face of mosaic graphite	
Transmission factor		0.08–0.43
μ , cm ⁻¹	135	116
Data collection method	θ - 2θ scan (1° /min along 2θ)	
Scan range	1° below K α_1 to 1° above K α_2	
Background counts, s	10	10
2θ limits, deg	3–55	3–60
Unique data used, $F_o^2 > 3\sigma(F_o^2)$	851	3206 (includes Friedel pairs)
Final no. of variables	24	140

removed from the drybox and connected to a high-vacuum line. The capillary was cooled to $-78^\circ C$, evacuated, and sealed. Crystals were grown inside the capillary by slow sublimation (6–24 h) using a microscope lamp focused on a colored card beneath the capillary as the heat source.

X-Ray Diffraction. A Picker FACS-I automated diffractometer equipped with a graphite monochromator and molybdenum tube was used for the unit-cell measurements and data collection, the details of which are shown in Table I.

For the $U(BH_4)_4 \cdot O(CH_3)_2$ experiments, the only suitable crystal found was an irregularly shaped one that had grown into the tip of the capillary. ω scans of several low-angle reflections showed widths at half-peak height of 0.13 – 0.22° with the latter along the c^* axis. Cell dimensions were obtained by a least-squares refinement procedure of the angular settings of 12 manually centered reflections for which 2θ was between 35 and 40° . A total of 3277 scans were measured and later averaged to give a set of 1402 unique reflections. Three standard reflections were measured after each 200th scan to monitor for crystal decay, instrumental stability, and crystal alignment. After 6 days of data-taking, the standards exhibited about 9% decay in their intensities, and the data were corrected accordingly. The crystal color had changed to brown. As the crystal had assumed the shape and distortions of the capillary tip, we were unable to describe the crystal shape in a manner suitable for our absorption program, and therefore no absorption correction was made.

For the $U(BH_4)_4 \cdot O(C_2H_5)_2$ experiment, a crystal, ~ 0.3 mm in size, was found in one of the capillaries. ω scans of several low-angle reflections showed widths at half-peak height of 0.17 – 0.27° with the latter along c^* ; the peaks were somewhat unsymmetrical but adequate for data collection. Cell dimensions were obtained from the angle settings of the (800), (005), and (0,16,0) reflections. A total of 4563 scans were measured and later averaged to give a set of 3902 unique reflections according to point group 2, or 2020 for point group $2/m$. Three standard reflections were measured after each 200th scan; after 8 days of data-taking, each standard exhibited about 8% decay in its intensity, and the data were corrected accordingly. The crystal color had changed to a deep red-brown. An absorption correction by an analytical integration¹¹ was made, and its validity tested on a set of intensity data at various azimuthal angles for several reflections in a diverse region of reciprocal space. The data were processed, averaged, and given estimated standard deviations using formulas

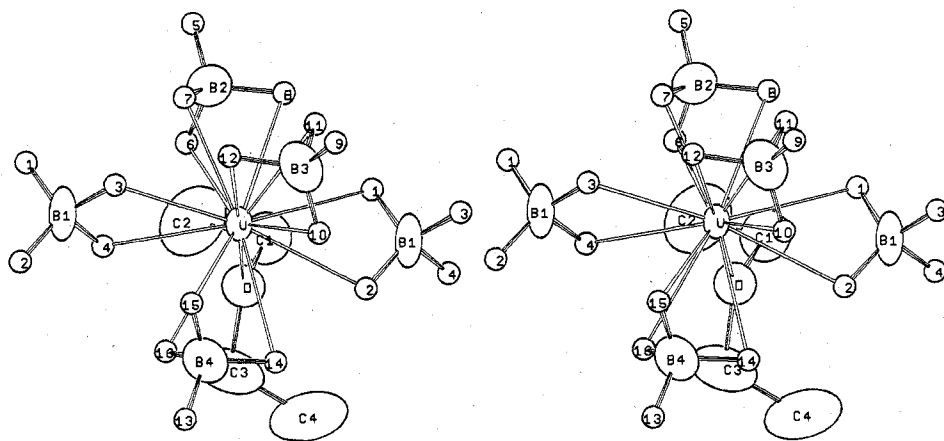


Figure 1. Stereogram (drawn with C. K. Johnson's ORTEP) of one unit of the ethyl ether complex, showing hydrogen positions and the atomic numbering. The methyl compound is numbered in an analogous manner, except that in it B(2) corresponds to both B(2) and B(4).

presented in the supplementary material. The factors $p = 0.06$ and $p = 0.025$ were used in the calculations of $\sigma(F^2)$ for the methyl and ethyl ether complexes, respectively.

The Patterson functions revealed the uranium atom positions and, in the case of the methyl ether adduct, most of the light-atom positions. Subsequent least-squares and difference-Fourier maps gave the positions of all the atoms except hydrogen. The structures were refined by full-matrix least squares where the function $\sum w(\Delta F)^2 / \sum wF_o^2$ was minimized. For the ethyl compound, the four strongest reflections (two Bijvoet pairs) were observed a few percent weaker than calculated, and they were deleted from the data set. Otherwise, no correction for extinction was indicated and none was made for either crystal. The scattering factors used were those of Doyle and Turner¹² for neutral boron, carbon, and oxygen and those of Cromer and Waber¹³ for the neutral uranium atom corrected for dispersion according to Cromer and Liberman.¹⁴ The uranium atoms were given anisotropic thermal parameters in both cases.

In the methyl ether complex, all of the light atoms were assigned isotropic thermal parameters as attempts at anisotropic refinement resulted in little improvement in the R factors and in widely divergent thermal parameters. This behavior we attribute to errors from the uncorrected absorption effects. Attempts to locate hydrogen atoms in the difference maps failed, and these atoms were not included in the calculations. The largest peak in the difference-Fourier map was $1.5 \text{ e}/\text{\AA}^3$ and was less than 0.4 \AA from B(1). The final R factor, $\sum |\Delta F| / \sum |F_o|$, was 0.036 for 851 data where $F^2 > 3\sigma$ and 0.076 for all 1402 data. The weighted R_w factor, $(\sum w(\Delta F)^2 / \sum wF_o^2)^{1/2}$, was 0.045. The standard deviation of an observation of unit weight was 1.03.

In the ethyl ether compound the nonhydrogen atoms were found by Fourier methods and refined by least squares, first using the data averaged according to $2/m$. Then the members of each Bijvoet pair were treated as independent observations (data averaged according to point group 2). The absolute configuration which is described by the tables and figures is the one which gave the better agreement after both alternatives had been tested.

A model for the hydrogen positions was derived, starting with the boron and oxygen positions and using the known structure¹⁵ of $U(BH_4)_4$ for guidance as to how the hydrogen atoms might pack around the uranium atom. A ΔF Fourier map, calculated after anisotropic refinement of the other atoms, showed positive densities in the anticipated locations with peak heights of $0.4\text{--}1.6 \text{ e}/\text{\AA}^3$. Attempts to locate the hydrogen atoms in the ethyl ether moiety failed, and these atoms were not included in the calculations. Because the borohydride hydrogen atoms were poorly resolved and because the map showed spurious peaks elsewhere of similar magnitude, we imposed restraints on the geometry of the borohydride groups in the following manner.¹⁶ Interatomic distances between selected atoms are introduced into the least-squares calculations and treated as observations; estimated standard deviations of these distances are also introduced and used to calculate the weights. Except that the derivatives of these distances with respect to the positional parameters are calculated by a special patch and that these "observations" are not included in the R values reported here, these terms are included in the least-squares calculation in the same manner as the observed

structure factors. This procedure allows the structure to adjust to the electron density with a flexibility governed by the weighting. All of the hydrogen distances were restrained to the following values: U-H to $2.4 \pm 0.2 \text{ \AA}$, B-H to $1.19 \pm 0.05 \text{ \AA}$, H-H to $1.94 \pm 0.05 \text{ \AA}$. These distances impose tetrahedral geometry on the BH_4^- ions but leave each one free to rotate about the U-B axis. One common isotropic thermal parameter was used for all 16 hydrogen atoms. The structure with these restraints was refined to convergence; R was 0.023 for 3210 data where $F^2 > 3\sigma$ and 0.036 for all 3902 data; R_w was 0.026.

Because we were interested in the experimental determination of the anomalous dispersion corrections, we modified our least-squares program to include f'' for uranium (the imaginary part of the dispersion correction) as one of the variables to be refined. The other variables, and the restraints on some of them, were the same as before. Refinement changed f'' from 9.654 (Cromer and Liberman¹⁴) to 3.9 (4) electrons. This discrepancy is far outside the error estimated for either value, and we attribute it to twinning of a mixture of right- and left-handed crystal domains, with the crystal containing about 70% of one enantiomer and 30% of the other. To a good approximation, because the dispersion effects are a small perturbation, a calculation with a weighted mean value of f'' is equivalent to a calculation of each twin component separately, followed by averaging of the intensities, which is the proper method for a twinned specimen.

The final R was 0.022 for 3206 reflections included in the refinement and 0.035 for 3898 data including those of zero weight, and the standard deviation of an observation of unit weight was 1.02.

Final positional and thermal parameters are given in Tables II and III. Tables of observed structure factor amplitudes are given in the supplementary material. Distances and angles are listed in Tables IV and V. The atom numbering is seen in Figure 1.

Discussion

The molecular structures of both of these etherates of uranium borohydride are related to that of uranium borohydride itself. In uranium borohydride¹⁵ the boron atoms are connected to uranium by a combination of triple- and double-hydrogen-bridge bonds. These two types of bridging bonds can be identified by the U-B interatomic distances of 2.5 and 2.9 \AA for the triple- and double-hydrogen-bridge bonds, respectively. The double-bridge bonds tie pairs of uranium atoms together, and in the case of uranium borohydride lead to a three-dimensional molecular network with a coordination of 14 hydrogen atoms about each uranium atom. In both the methyl and ethyl ether compounds the structures consist of infinite linear chains of uranium and boron atoms hooked together by double-hydrogen-bridge bonds, as shown in Figures 1-3. Each uranium atom has 13 hydrogens and 1 oxygen atom in its coordination sphere yielding a total of 14, the same as in uranium borohydride. In the methyl complex the ethers are alternately on one side or the other of the chain, whereas in the ethyl ether complex they are all on the same side. The ether moieties are coordinated to the uranium atom by their oxygen atoms at 2.44 and 2.49 \AA , respectively, for the methyl

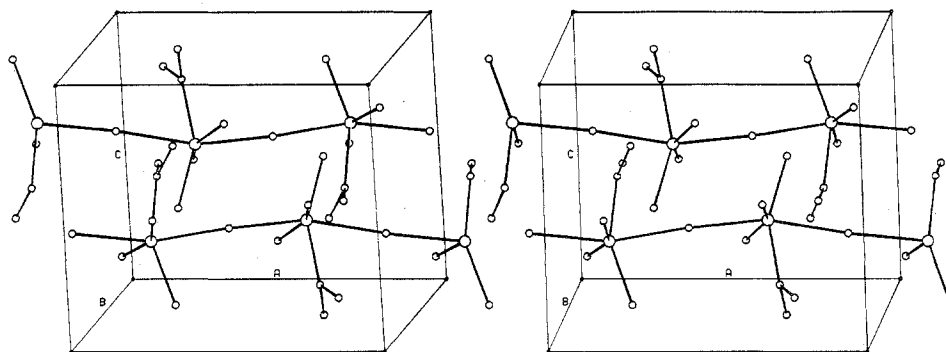


Figure 2. Stereogram showing the chain structure in $U(BH_4)_4 \cdot O(CH_3)_2$.

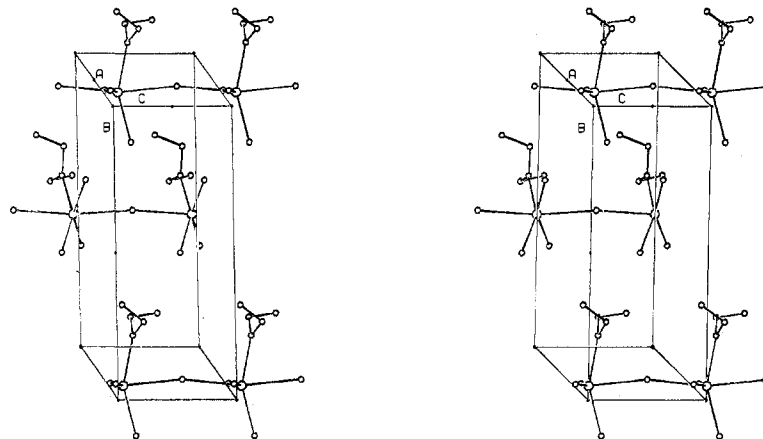


Figure 3. Stereogram showing the chain structure in $U(BH_4)_4 \cdot O(C_2H_5)_2$.

Table II. Positional and Thermal Parameters for $U(BH_4)_4 \cdot O(CH_3)_2$ ^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
U	0.11737 (4)	0.25	0.21009 (6)	<i>b</i>
O	0.1483 (9)	0.25	0.453 (1)	4.5 (2)
B(1)	-0.133 (2)	0.25	0.240 (3)	6.5 (6)
B(2)	0.073 (2)	0.494 (2)	0.220 (2)	7.0 (4)
B(3)	0.184 (3)	0.25	-0.029 (4)	7.7 (7)
C	0.180 (3)	0.368 (3)	0.534 (4)	17.9 (10)

^a The anisotropic temperature factor has the form $\exp(-0.25(B_{11}h^2a^* + 2B_{12}hka^*b^* + \dots))$. The isotropic temperature factor has the form $\exp(-B((\sin \theta)/\lambda)^2)$. ^b $B_{11} = 1.69$ (2); $B_{22} = 5.32$ (3); $B_{33} = 3.22$ (2); $B_{12} = 0$; $B_{13} = -0.08$ (3); $B_{23} = 0$.

and ethyl ether. Because of the lack of an absorption correction for the methyl compound, we doubt that this difference is significant.

In both compounds the boron and oxygen atoms are arranged around uranium in an octahedral manner, but O-U-B and B-U-B angles deviate by as much as 26° from the regular values of 90 and 180°. Corresponding angles for the two compounds agree within about 3° or better (Table V). It seems clear that this distortion is the result of the packing requirements for the hydrogen atoms around the uranium. Bernstein et al.¹⁵ gave a similar interpretation to the structure of crystalline $U(BH_4)_4$, where the situation is analogous.

We refined the hydrogen coordinates only for the ethyl compound, but because of the similarity of the angles noted above we assume that in the methyl compound the hydrogen configuration is the same. In the ethyl compound the oxygen atom and 13 hydrogen atoms, which surround one uranium atom, can be described by the corners of a polyhedron with 14 triangular and 5 quadrilateral faces (Figure 4), if one overlooks slight deviations from planarity of the atoms at the corners of each quadrilateral face. This solid is topologically

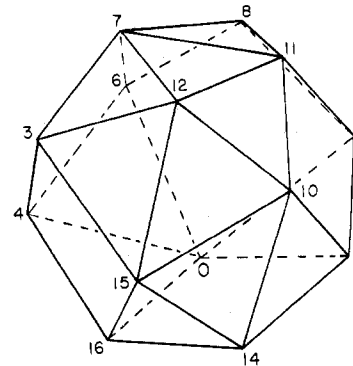


Figure 4. Coordination polyhedron of uranium in the ethyl complex. The numbers identify the hydrogen atoms, and O indicates oxygen.

distinct from the one which corresponds to the 14 hydrogen neighbors of uranium in $U(BH_4)_4$, described as approximately a bicapped hexagonal antiprism,¹⁵ but some fragments of the two solids are similar. The oxygen atom has 5 hydrogen neighbors with O-U-H angles between 68 and 72°. Each of the 13 hydrogen atoms in the coordination sphere has either 4 or 5 neighbors (O + 3 H, 4 H, or 5 H). The H-U-H angles are 46–53° when the hydrogen atoms are in the same borohydride ion; otherwise they range from 50 to 67°.

Absolute Configuration and Anomalous Dispersion. In discussions of absolute configuration the possibility of twinning of enantiomers is often disregarded. This is appropriate if it is known that the crystal consists of pure enantiomeric molecules, as is often true with materials of biological origin. However, the present case may serve as a reminder that twinning is always possible when the asymmetry exists in the crystal structure but not in its component molecules. This possibility of twinning seriously undermines the validity of a statistical probability test applied to the binary choice of one

Table III. Positional and Thermal Parameters for $U(BH_4)_4 \cdot O(C_2H_5)_2^a$

Atom	x	y	z	Atom	x	y	z
U	0.26472 (2)	0	0.12412 (3)	H(4)	0.318 (8)	-0.078 (3)	0.784 (9)
B(1)	0.287 (1)	-0.0189 (6)	0.632 (1)	H(5)	0.706 (5)	0.076 (4)	0.16 (1)
B(2)	0.577 (1)	0.0501 (6)	0.157 (2)	H(6)	0.532 (7)	-0.021 (2)	0.10 (1)
B(3)	0.156 (1)	0.1501 (5)	0.193 (2)	H(7)	0.455 (6)	0.090 (4)	0.02 (1)
B(4)	-0.037 (1)	-0.0621 (7)	-0.080 (2)	H(8)	0.553 (7)	0.059 (4)	0.359 (7)
O	0.3723 (6)	-0.1508 (3)	0.2466 (8)	H(9)	0.106 (7)	0.214 (3)	0.24 (1)
C(1)	0.5516 (9)	-0.1645 (5)	0.397 (2)	H(10)	0.072 (7)	0.090 (3)	0.23 (1)
C(2)	0.662 (2)	-0.2037 (8)	0.249 (3)	H(11)	0.309 (5)	0.136 (4)	0.31 (1)
C(3)	0.271 (1)	-0.2325 (6)	0.197 (2)	H(12)	0.168 (8)	0.144 (4)	-0.005 (7)
C(4)	0.202 (2)	-0.259 (1)	0.405 (3)	H(13)	-0.179 (5)	-0.081 (4)	-0.19 (1)
H(1)	0.416 (5)	-0.009 (5)	0.578 (8)	H(14)	-0.015 (7)	-0.061 (4)	0.130 (6)
H(2)	0.173 (6)	-0.039 (3)	0.467 (8)	H(15)	-0.008 (6)	0.011 (3)	-0.14 (1)
H(3)	0.265 (8)	0.043 (3)	0.75 (1)	H(16)	0.072 (6)	-0.107 (3)	-0.13 (1)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	2.837 (7)	2.708 (6)	1.471 (5)	-0.28 (3)	0.683 (4)	-0.10 (4)
B(1)	4.6 (3)	6.0 (8)	2.1 (2)	0.1 (3)	1.3 (2)	-0.6 (3)
B(2)	3.8 (3)	5.3 (4)	4.5 (4)	-0.9 (3)	1.3 (3)	-0.2 (3)
B(3)	5.7 (4)	3.9 (3)	4.4 (4)	0.7 (3)	1.2 (3)	-0.9 (3)
B(4)	4.1 (3)	6.6 (5)	3.8 (4)	-1.2 (3)	0.1 (3)	-0.6 (3)
O	4.4 (2)	3.2 (2)	3.6 (2)	0.0 (1)	0.8 (2)	0.3 (1)
C(1)	4.2 (3)	5.2 (3)	5.0 (4)	1.4 (3)	0.7 (3)	1.0 (3)
C(2)	7.9 (6)	7.7 (6)	10.7 (9)	3.5 (5)	4.5 (6)	1.6 (6)
C(3)	7.7 (6)	4.3 (4)	7.9 (6)	-1.6 (3)	-0.7 (5)	0.3 (4)
C(4)	10.1 (8)	8.7 (7)	12.0 (12)	-3.4 (6)	3.0 (8)	2.7 (7)

^a The estimated standard deviations for the hydrogen atoms are the result of least-squares refinement on a model in which the hydrogen distances were restrained as described in the text. One isotropic thermal parameter was applied to all of the hydrogens, and it refined to 4.5 (4) Å².

Table IV. Distances (Å) in $U(BH_4)_4 \cdot O(CH_3)_2$ and $U(BH_4)_4 \cdot O(C_2H_5)_2$

	Methyl compd	Ethyl compd
U-O	2.44 (1)	2.485 (5)
U-B(1)	2.87 (2)	2.89 (1)
U-B(1) ^a	2.90 (2)	2.89 (1)
U-B(2)	2.53 (2)	2.55 (1)
U-B(4)	(2.53)	2.55 (1)
U-B(3)	2.49 (4)	2.52 (1)
O-C(1)	1.48 (4)	1.46 (1)
O-C(3)	(1.48)	1.47 (1)
C(1)-C(2)		1.51 (1)
C(3)-C(4)		1.50 (2)

Ethyl Compound			
U-H(1)	2.55 (5)	B(1)-H(1)	1.16 (3)
-H(2)	2.36 (5)	-H(2)	1.15 (3)
-H(3) ^a	2.26 (6)	-H(3)	1.20 (3)
-H(4) ^a	2.42 (6)	-H(4)	1.23 (3)
		B(2)-H(5)	1.10 (3)
-H(6)	2.19 (6)	-H(6)	1.16 (3)
-H(7)	2.25 (6)	-H(7)	1.24 (3)
-H(8)	2.48 (6)	-H(8)	1.24 (3)
		B(3)-H(9)	1.12 (3)
-H(10)	2.27 (6)	-H(10)	1.19 (3)
-H(11)	2.32 (6)	-H(11)	1.24 (3)
-H(12)	2.38 (6)	-H(12)	1.17 (3)
		B(4)-H(13)	1.17 (3)
-H(14)	2.42 (6)	-H(14)	1.17 (3)
-H(15)	2.29 (6)	-H(15)	1.21 (4)
-H(16)	2.44 (6)	-H(16)	1.21 (3)

^a Symmetry operations: methyl compound, $1/2 + x, 1/4, 1/2 - z$; ethyl compound, $x, y, z - 1$.

configuration or the other. In the present case one configuration fits the data significantly better than does the other, but the twinning model fits still better.

The configuration of a particular specimen in a case like this is not intrinsically of general significance. It is important, however, in connection with the "polar dispersion error" which involves serious errors in atomic coordinates when structures are refined in polar space groups with data sets which are incomplete in the Bijvoet sense and with a model which is incorrect with respect to configuration or anomalous dispersion

Table V. Angles (deg) in $U(BH_4)_4 \cdot O(CH_3)_2$ and $U(BH_4)_4 \cdot O(C_2H_5)_2$

	Methyl compd	Ethyl compd
O-U-B(1)	92.4 (6)	94.3 (2)
-B(1) ^a	71.8 (6)	72.6 (2)
-B(2)	89.4 (5)	90.2 (3)
-B(4)	(89.4)	89.6 (3)
-B(3)	153.9 (8)	154.6 (3)
B(1)-U-B(1) ^a	164.24 (4)	166.7 (4)
-B(2)	78.4 (5)	77.3 (3)
-B(4)	(78.4)	79.5 (3)
-B(3)	113.7 (9)	111.2 (3)
B(1) ^a -U-B(2)	100.9 (5)	99.6 (3)
-B(4)	(100.9)	102.5 (3)
-B(3)	82.1 (9)	82.0 (3)
B(2)-U-B(4)	(157 (1))	156.8 (3)
-B(3)	95.7 (5)	94.9 (3)
B(3)-U-B(4)	(95.7)	95.2 (3)
U-O-C(1)	125 (2)	120.2 (4)
-C(3)	(125)	127.1 (5)
C(1)-O-C(3)	107 (3)	112.6 (6)
O-C(1)-C(2)		110.4 (8)
O-C(3)-C(4)		112 (1)
U-B(1) ^a -U ^a	176 (1)	166.7 (4)

^a Symmetry operations: methyl compound, $1/2 + x, 1/4, 1/2 - z$; ethyl compound, $x, y, z - 1$.

terms or both.^{17,18} In our case, because complete data were used in the refinement, the interatomic distances differ by trivial amounts regardless of which assumption was made about configuration. However, thermal parameters are strongly correlated with f'' and vary by several standard deviations among the different models.

Registry No. $U(BH_4)_4 \cdot O(CH_3)_2$, 65150-32-5; $U(BH_4)_4 \cdot O(C_2H_5)_2$, 65150-21-2; $U(BH_4)_4$, 38903-76-3.

Supplementary Material Available: Formulas used in data reduction and listings of the structure factors (22 pages). Ordering information is given on any current masthead page.

References and Notes

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Contribution from the Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720

Preparation and Crystal Structure of Uranium(IV) Borohydride-Bis(tetrahydrofuran), $\text{U}(\text{BH}_4)_4 \cdot 2\text{OC}_4\text{H}_8$ ¹

RICHARD R. RIETZ, NORMAN M. EDELSTEIN,* HELENA W. RUBEN, DAVID H. TEMPLETON,*
and ALLAN ZALKIN*

Received July 27, 1977

Uranium(IV) borohydride reacts quantitatively with tetrahydrofuran to form $\text{U}(\text{BH}_4)_4 \cdot 2\text{OC}_4\text{H}_8$, a pale green solid which has been characterized by single-crystal x-ray diffractometry. This air- and moisture-sensitive compound can be sublimed at $50\text{--}60^{\circ}\text{C}$ and 10^{-5} mm. $\text{U}(\text{BH}_4)_4 \cdot 2\text{OC}_4\text{H}_8$ is orthorhombic with $a = 7.134(4) \text{ \AA}$, $b = 11.311(6) \text{ \AA}$, $c = 10.442(7) \text{ \AA}$, and $Z = 2$, ($d_x = 1.74 \text{ g cm}^{-3}$). The space group is $Pnc2$ or $Pnmc$. For 789 data, where $I > 2\sigma$, the structure refined to $R = 0.027$ and $R_w = 0.032$ in space group $Pnmc$, with disorder in both the THF and boron positions. The complex is a monomer with a distorted-octahedral arrangement about the uranium of four borohydride groups and two THF molecules. The U-O distance is $2.47(1) \text{ \AA}$. The U-B distance of $2.56(4) \text{ \AA}$ is characteristic of the triple-hydrogen-bridge bonds found in uranium(IV) borohydride. A configuration is assigned to the hydrogen atoms which places 12 of them at the corners of an hexagonal antiprism, capped by the two oxygen atoms of THF, giving the uranium atom 14 nearest neighbors. This compound is the only known uranium borohydride complex which is monomeric in the solid state.

Introduction

Interest in the preparation and characterization of new volatile actinide compounds prompted us to reinvestigate the chemistry of uranium(IV) borohydride. In a study of Lewis-base derivatives of $\text{U}(\text{BH}_4)_4$,² we synthesized a number of new volatile compounds. The methyl and ethyl etherates of $\text{U}(\text{BH}_4)_4$ have been characterized as monoetherates which form linear polymers in the crystalline state.³ We report here on the tetrahydrofuran complex of $\text{U}(\text{BH}_4)_4$ which is a dietherate and is monomeric in the crystalline state.

Experimental Section

Materials and Chemical Techniques. $\text{U}(\text{BH}_4)_4$ was prepared by the method of Schlesinger and Brown⁴ and purified by sublimation at $30\text{--}40^{\circ}\text{C}$ and 10^{-5} mm. Tetrahydrofuran (Aldrich) was doubly distilled from sodium/benzophenone under argon. All manipulations were performed in Pyrex high-vacuum lines free of mercury, oil, and grease or in argon-filled dryboxes.⁵

Preparation of $\text{U}(\text{BH}_4)_4 \cdot 2\text{THF}$. In a typical preparation, 0.206 g of $\text{U}(\text{BH}_4)_4$ (0.69 mmol) was sublimed into a 50-mL trap at -78°C . THF (1.76 g) was condensed on top of the $\text{U}(\text{BH}_4)_4$. The trap was sealed and warmed to 20°C with shaking. The $\text{U}(\text{BH}_4)_4$ first lightened in color and then dissolved to give a green solution. The excess THF was removed by pumping at -45°C for 4 h. The remaining green solid was quantitatively recovered by sublimation in bulk at $50\text{--}60^{\circ}\text{C}$ to a -78°C cold finger. The pale green crystals (mp 122°C dec, sealed capillary) decompose slowly in air but explode into flames when touched with a drop of water. The solid has been stored under argon or in vacuum for several months with only minor decomposition. Additional physical and spectroscopic data will appear elsewhere.²

Crystal Growth. Crystals taken directly from the sublimator and sealed in capillaries were found to be unsuitable for study. Instead, several crystals were ground in a mortar and pestle and poured into a capillary drawn from a 14/35 quartz joint. An adapter containing a stopcock to trap argon over the sample was placed on the loaded joint. This assembly was removed from the drybox and connected to a high-vacuum line. The capillary was cooled to -78°C , evacuated, and sealed. Crystals were grown inside the capillary by slow sublimation (6–24 h) using a microscope lamp focused on a colored card beneath the capillary as the heat source. After several dozen attempts, a pale green transparent tabular crystal was obtained.

Data Collection, Reduction, and Refinement. The crystal was placed on a Picker FACS-I automatic diffractometer equipped with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda(\text{K}\alpha_1) 0.70926 \text{ \AA}$) for study. Cell dimensions obtained from carefully centered settings on the $\text{K}\alpha_1$ peaks of the 800, $\bar{8}00$, 0,12,0, 0, $\bar{1}2$,0, 0,0,12, and 0,0, $\bar{1}2$ reflections are $a = 7.134(4) \text{ \AA}$, $b = 11.311(6) \text{ \AA}$, and $c = 10.442(7) \text{ \AA}$; for two molecules in the unit cell, the density is 1.74 g cm^{-3} . The widths of the ω scans at half-height were typically 0.1° . The pattern of intensities showed a very pronounced pseudo- A -centering which was indicative of the uranium atom on the origin. Intensity data were collected with the θ - 2θ scan method where each reflection was scanned from 0.55° before the $\text{K}\alpha_1$ to 0.55° beyond the $\text{K}\alpha_2$ peak; 4-s backgrounds were measured at each end of the scan. All of the data with zero and positive k indices were collected to a 2θ angle of 30° , and only the A -centered data were collected from 30 to 60° ; beyond 30° the weak non- A -centered reflections were unobservable. The temperature was $23.5 \pm 1.0^{\circ}\text{C}$. Three standards were measured after each 200th reflection, and no observable decay in these standards was noted. The formulas used to process the data are presented in the supplementary material. An ignorance factor of $p = 0.04$ was applied. The 3763 measured intensities resulted in 915 unique reflections; 160