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Preparation and Crystal Structure of Uranium(IV) Borohydride–Bis(tetrahydrofuran), $U(BH_4)_4 \cdot 2OC_4H_8$[1]

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Received July 27, 1977

Uranium(IV) borohydride reacts quantitatively with tetrahydrofuran to form $U(BH_4)_4 \cdot 2OC_4H_8$, a pale green solid which has been characterized by single-crystal x-ray diffractometry. This air- and moisture-sensitive compound can be sublimed at 50–60 °C and 10^{-5} mm. $U(BH_4)_4 \cdot 2OC_4H_8$ is orthorhombic with $a = 7.134$ (4) Å, $b = 11.311$ (6) Å, $c = 10.442$ (7) Å, and $Z = 2$, ($d_x = 1.74$ g cm^{-3}). The space group is *Pnc*2 or *Pncm*. For 789 data, where $I > 2\sigma$, the structure refined to $R = 0.027$ and $R_w = 0.032$ in space group *Pncm*, 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) Å. The U–B distance of 2.56 (4) Å 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 $U(BH_4)_4$,[2] we synthesized a number of new volatile compounds. The methyl and ethyl etherates of $U(BH_4)_4$ have been characterized as monoetherates which form linear polymers in the crystalline state.[3] We report here on the tetrahydrofuran complex of $U(BH_4)_4$ which is a dietherate and is monomeric in the crystalline state.

Experimental Section

Materials and Chemical Techniques. $U(BH_4)_4$ was prepared by the method of Schlesinger and Brown[4] and purified by sublimation at 30–40 °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 $U(BH_4)_4 \cdot 2THF$. In a typical preparation, 0.206 g of $U(BH_4)_4$ (0.69 mmol) was sublimed into a 50-mL trap at −78 °C. THF (1.76 g) was condensed on top of the $U(BH_4)_4$. The trap was sealed and warmed to 20 °C with shaking. The $U(BH_4)_4$ 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 50–60 °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 sublimer 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 Mo Kα radiation (λ(Kα_1) 0.70926 Å) for study. Cell dimensions obtained from carefully centered settings on the Kα_1 peaks of the 800, $\bar{8}00$, 0,12,0, 0,$\overline{12}$,0, 0,0,12, and 0,0,$\overline{12}$ reflections are $a = 7.134$ (4) Å, $b = 11.311$ (6) Å, and $c = 10.442$ (7) Å; 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 Kα_1 to 0.55° beyond the Kα_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 ± 1.0 °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

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Table I. Positional and Thermal Parameters[a]

Atom	x	y	z
U	0	0	0
O	0.1618 (9)	0.1931 (6)	0
C(1)	0.077 (2)	0.313 (1)	0
C(2)	0.223 (3)	0.399 (1)	0
C(3)	0.397 (2)	0.340 (1)	0
C(4)	0.362 (2)	0.217 (1)	0
B(1)	0.242 (3)	−0.046 (2)	0.179 (2)
B(2)	0.197 (2)	−0.106 (1)	0.164 (2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}
U	3.13 (1)	2.93 (1)	3.79 (2)	−0.04 (5)
O	3.6 (3)	2.8 (2)	6.1 (4)	−0.1 (2)
C(1)	5.5 (5)	3.6 (5)	11.9 (12)	1.0 (4)
C(2)	6.4 (8)	3.6 (5)	21.5 (24)	−0.2 (5)
C(3)	5.6 (7)	6.2 (7)	11.5 (12)	−2.6 (6)
C(4)	3.9 (6)	4.4 (6)	30.8 (31)	−1.5 (5)
B(1)	$B = 5.0$ (3) A^2			
B(2)	$B = 4.3$ (3) A^2			

[a] The anisotropic temperature factor has the form $\exp(-0.25 \cdot (B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots))$. Because of the mirror plane, $B_{13} = B_{23} = 0$. The isotropic temperature factor has the form $\exp(-B((\sin\theta)/\lambda)^2)$.

Table II. Interatomic Distances (A)

U–2O	2.47 (1)	O–C(4)	1.45 (2)
U–4B(1)[a]	2.60 (2)	C(1)–C(2)	1.43 (2)
U–4B(2)[a]	2.52 (2)	C(2)–C(3)	1.41 (2)
B(1)–B(2)	0.76 (2)	C(3)–C(4)	1.42 (2)
O–C(1)	1.48 (2)		

[a] B(1) and B(2) are the two positions occupied by the disordered boron atoms in the structure.

Table III. Angles (deg)

O–U–O[b]	180.0	U–O–C(1)	128.1 (7)
O–U–B(1)[a]	82.4 (5)	U–O–C(4)	128.4 (7)
O–U–B(2)[a]	80.8 (4)	C(1)–O–C(4)	103.5 (9)
B(1)–U–B(1)[d]	87.9 (9)	O–C(1)–C(2)	109 (1)
B(2)[b]–U–B(2)[c]	94.2 (8)	C(1)–C(2)–C(3)	108 (1)
B(1)–U–B(2)[c]	91.3 (6)	C(2)–C(3)–C(4)	108 (1)
B(1)–U–B(2)[b]	163.0 (5)	C(3)–C(4)–O	111 (1)

[a] See footnote *a* in Table II. [b] Symmetry operation $\bar{x}, \bar{y}, \bar{z}$. [c] Symmetry operation $x, y, \bar{z}$. [d] Symmetry operation $\bar{x}, \bar{y}, z$.

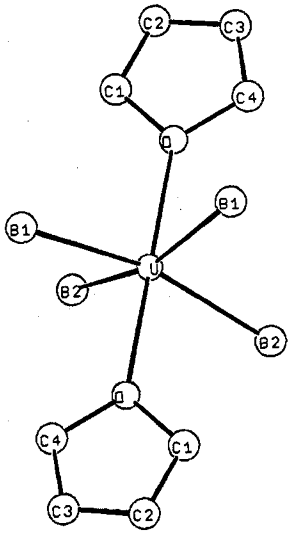

Figure 1. Structure of the $U(BH_4)_4 \cdot 2THF$ molecule. The tetrahydrofuran rings, which are shown as planar, represent the average positions of the atoms. The boron atoms are shown in one conformation of the disorder model.

of these were the weak non-*A*-centered type, half of which had intensities less than $\sigma(I)$.

An absorption correction was made,[6] $\mu = 92$ cm^{-1}, and correction factors varied from 3.3 to 6.4. The crystal was described by 6 crystal faces, 011, 0$\bar{1}\bar{1}$, 01$\bar{1}$, 0$\bar{1}$1, 100, and $\bar{1}$00. The crystal dimensions were 0.22 × 0.27 × 0.13 mm in the 011, 01$\bar{1}$, and 100 directions, respectively; the crystal volume was 0.0077 mm^3. Several azimuthal scans in diverse regions of reciprocal space were performed to test the validity of the absorption correction and to make minor adjustments on the crystal dimensions.

Space Group and Disorder. Our data are ambiguous with respect to the space group. The diffraction symmetry and the reflections which are systematically absent are consistent with either *Pncm*[7] (centric) or *Pnc*2 (noncentric). A search for Bijvoet differences revealed none which were significantly larger than the differences between equivalent reflections, but for this crystal the differences are expected to be small. For the reflections with $k + l$ even, which constitute most of the data, the centric uranium structure and the at least nearly centric tetrahydrofuran structure dominate the structure factor. For the reflections with $k + l$ odd, uranium makes no contribution, and its anomalous dispersion cannot give rise to a Bijvoet difference.

As the structure determination proceeded, it became clear that there was disorder of the conformation of the tetrahydrofuran ring, as is generally true of this molecule in crystals.[8-15] In space group *Pncm*, the THF ring lies in the mirror plane, and the disorder consists of displacements of atoms from this plane equally in either direction. Space group *Pnc*2 permits unsymmetrical displacements, but several attempts at refinement of various models failed to yield any significant improvement over centric models.

Fourier maps calculated for *Pncm* require the boron atoms to be distributed between pairs of sites, about 0.76 Å apart. The noncentric space group permits assignment of boron atoms to half of these sites in an ordered manner, described below, which corresponds to a molecular structure with very plausible packing of the hydrogen atoms. For this reason we prefer *Pnc*2 as a description of the structure. However, we carried out the final refinement in space group *Pncm* to avoid the several ambiguities inherent in the unsymmetrical disorder models and to gain a much better rate of convergence. The resulting coordinates for boron atoms should be nearly the same for either space group because the high-angle data are exclusively of the type $k + l$ even. For these reflections, the magnitudes of a structure factor, calculated for a noncentric structure and for a superposition of that structure and its inverse, are rarely different by 1% and never by as much as 2% for the models which we refined. Several noncentric refinements, with different models for the THF, gave coordinates for boron within one standard deviation of those reported here.

Structure Refinement. A trial structure, obtained from a three-dimensional Patterson map, was refined by full-matrix least squares in the centric space group *Pncm*. Anisotropic thermal parameters were applied first to the uranium atom only. Because the observed values of the larger intensities were consistently below the calculated values, an empirical extinction correction was applied where $F_{cor} = F_{obsd}(1 + 5 \times 10^{-7}I)$; F_{cor} and F_{obsd} are the corrected and observed structure factors, and I is the observed intensity. The largest correction factor was 1.19. The $R = \sum||F_o| - |F_c||/\sum|F_o|$ at this stage was 0.037 for 789 data with $F^2 > 2\sigma$. The planar THF molecule had chemically unreasonable bond distances which suggested disorder. A difference-Fourier map showed disorder not only in the THF molecule but also in the boron positions. Efforts to resolve the disorder into a double set of discrete atoms for the THF molecule failed, and so the THF molecule was refined with anisotropic thermal parameters. The boron atoms were refined as two half-atoms with isotropic thermal parameters. Hydrogen atoms were not observed and not included in the refinement. The final R factor was 0.027 for 789 data where $I > 2\sigma$ and 0.037 for all 915 data. $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ was 0.032. The standard deviation of a reflection of unit weight was 1.16.

The atomic parameters are given in Table I, and the distances and angles in Tables II and III.

Discussion

The structure consists of monomeric units of $U(BH_4)_4 \cdot 2OC_4H_8$. The borohydride and THF ligands form a distorted octahedron about the uranium atom; see Figure 1. The U–B distance is characteristic of the "terminal" borohydride found in $U(BH_4)_4$[16] where three hydrogen atoms from the borohydride ion contact the uranium atom. There are 14 neighbors

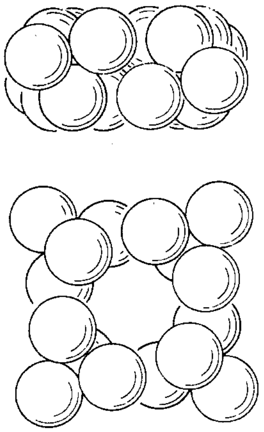

Figure 2. Structure proposed for the hydrogen atoms around each uranium atom. A boron atom (not shown) is at the center of each tetrahedron of hydrogen atoms; the view at the top shows how the boron atoms are alternately to either side of the central plane.

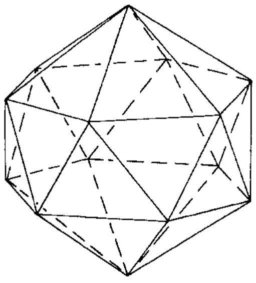

Figure 3. Coordination polyhedron for uranium. Hydrogen atoms, as shown in Figure 2, are at the corners of the central hexagonal antiprism, while oxygen atoms are at the top and bottom vertices.

to the uranium atom, consisting of 12 hydrogen and 2 oxygen atoms. Fourteen-coordination is also observed in $U(BH_4)_4$,[16] $U(BH_4)_4{\cdot}O(CH_3)_2$,[3] and $U(BH_4)_4{\cdot}O(C_2H_5)_2$.[3]

The BH_4^- bonding in this molecule is similar to that found for $U(BH_4)_4$ in the gaseous phase by analysis of infrared spectra[17,18] in that each boron has triple-hydrogen bridges to a single uranium atom. Upon subliming, $U(BH_4)_4$ converts from the 14-coordinate polymeric solid-state structure to the 12-coordinate monomeric structure. $U(BH_4)_4{\cdot}2OC_4H_8$ is the only uranium borohydride complex known to us which is monomeric in the solid state. However, $U(BH_4)_4$ has the monomeric structure in dilute mixed crystals with $Zn(BH_4)_4$ or $Hf(BH_4)_4$, which themselves are monomeric.[19]

The hydrogen atoms can be fit around the uranium atom very neatly in the configuration shown in Figure 2. This arrangement places the 12 hydrogen neighbors at the corners of a hexagonal antiprism, with oxygen atoms capping each hexagonal face (Figure 3). If these figures are constructed with tetrahedral BH_4^- ions and with oxygen equidistant from its six nearest hydrogen neighbors, one calculates O–U–B angles of 83 and 97°, with boron atoms alternately above and below the equatorial plane (oxygen atoms at the poles). The calculations in space group *Pnc*2 give just this conformation, with O–U–B angles of 81, 82, 99, and 98°. The O–U–B angles can be fit exactly with very minor adjustments of the hydrogen positions. One calculates other angles O–U–H = 68°, H–U–H = 49° (hydrogen atoms in the same borohydride ion), and H–U–H = 57 or 58° (hydrogen atoms in neighboring ions). These values are well within the ranges for corresponding ones observed in the structure of the diethyl ether complex of uranium borohydride.[3] The bicapped hexagonal antiprism which we propose here is the same polyhedron which was chosen as an approximation to describe the 14 hydrogen neighbors of uranium in the structure of $U(BH_4)_4$.[16]

The above structure for the complex is that corresponding to space group *Pnc*2. In the centric group these complexes are mixed randomly with others which are inverted through the uranium atom.

The disorder of the THF molecule seems to be independent of the possible disorder of the borohydride configuration. The bond lengths are calculated shorter than is chemically reasonable, and large B_{33} thermal parameters indicate significant displacements from the planar structure imposed by the model. Both of these characteristics are commonplace of this molecule as observed in many other crystals,[8-15] and we have been unable to find an example of a crystal structure in which it exists with good bond lengths and small amplitudes of motion. It is a flexible molecule with many conformations of nearly equal energy, and it has a mode of motion, referred to as "pseudorotation", in which a flexing of the ring carries angular momentum.[20] We made several attempts to describe it as a mixture of two conformations, in both the centric and the noncentric space groups, without finding any significantly better model. Evidently more conformations are important, but the diffraction data do not justify a more elaborate model.

The monomer units pack in the crystal in a manner which corresponds nearly to a simple cubic lattice. Each molecule has six neighbors, two at 7.13 Å and four at 7.70 Å (measured between uranium atoms), in directions parallel to *a* and to the *b*–*c* diagonals.

Registry No. $U(BH_4)_4$, 38903-76-3; $U(BH_4)_4{\cdot}2THF$, 65167-99-9.

Supplementary Material Available: Data processing formulas and a listing of observed structure factors (5 pages). Ordering information is given on any current masthead page.

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