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Preparation and Crystal Structures of Tetrakis(methyltrihydroborato)uranium(IV)bis(tetrahydrofuranate) and Tetrakis(methyltrihydroborato)uranium(IV)tetrahydrothiophenate*

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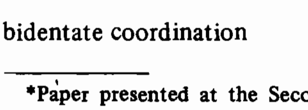
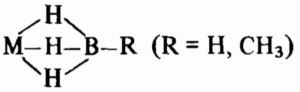
Summary. The U(IV) complexes, $U(BH_3CH_3)_4 \cdot 2OC_4H_8$ and $[U(BH_3CH_3)_4 \cdot SC_4H_8]_2$, have been prepared and their structures determined. Crystals of $(BH_3CH_3)_4U \cdot 2OC_4H_8$ are orthorhombic, *Aba*2, with $a = 12.911(3)$, $b = 16.072(4)$, $c = 10.116(4)$ Å, at 23 °C. For $Z = 2$ the calculated density is 1.574 g/cm^3. Crystals of $[(CH_3BH_3)_4U \cdot SC_4H_8]_2$ are monoclinic, $P2_1/c$, with $a = 12.054(2)$, $b = 16.372(3)$, $c = 18.545(3)$ Å and $\beta = 108.82(2)°$ at 23 °C. For $Z = 4$ the calculated density is 1.694 g/cm^3. The structures were refined by full-matrix least-squares to a conventional *R* factor of 0.028, [1378 data, $F^2 > 2\sigma(F^2)$] for the tetrahydrofuran complex, and 0.038 [2732 data, $F^2 > 2\sigma F^2$] for the tetrahydrothiophen plex. The tetrahydrofuran complex is monomolecular with the uranium atom on a two-fold axis and coordinated to four methyltrihydroborato and two tetrahydrofuran ligands; the U–B distances are 2.55(2) and 2.58(2) Å, and the U–O distance is 2.485(6) Å. The tetrahydrothiophene complex is a dimer in which two sulfur atoms bridge the uranium atoms of two tetra(methyltrihydroborato)uranium(IV) molecules; the U–B distances range from 2.468(2) to 2.591(2) Å, and the U–S distances are 3.120(4) and 3.239(5) Å; the S–S and U–U distances in the bridge are 3.477(5) and 5.374(1) Å, respectively.

Introduction

Structural studies of actinide(IV)tetrahydroborate and -methyltrihydroborate complexes have been reported [1–5]. Typically the tetrahydroborate or methyltrihydroborate group is coordinated to the metal through bidentate or tridentate ligation:

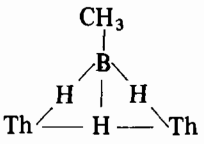


bidentate coordination



tridentate coordination

In the case of the actinide(IV)tetrahydroborate complexes, the bidentate bridge often links two adjacent metal atoms. Examples include $U(BH_4)_4$ [1], $U(BH_4)_4 \cdot OMe_2$ [2a], $U(BH_4)_4 \cdot OEt_2$ [2a], and $U(BH_4)_4 \cdot O(n\text{-}Pr)_2$ [2c]. In the dimeric complexes, $[Th(BH_3CH_3)_4]_2 \cdot OEt_2$ and $[Th(BH_3CH_3)_4 \cdot THF]_2$ [5c], the methyltrihydroborate ligand serves in a unique bridging capacity since it cannot form bidentate hydrogen bridges between adjacent metal atoms as in the actinide(IV)tetrahydroborate complexes.* The Th atoms are linked by a Th–H–BH(CH$_3$)–H–Th bridge, with the unique hydrogen atom directly bridging the two Th atoms:



This type of bridging is similar to that found in the complex, $Co_6(BH_4)_2[Ph_2P(CH_2)_5PPh_2]_2 \cdot 0.5(C_6H_6)$ [6] and occurs when the coordination sphere about the metal ion is not saturated.

In order to explore further the coordination geometry of the $BH_3CH_3^-$ ligand, we have prepared several other mono-base adducts of $Th(BH_3CH_3)_4$ and $U(BH_3CH_3)_4$ as well as some bis-base adducts [5d]. In this paper we report the synthesis and crystal structures of two uranium(IV)methyltrihydroborate complexes, $U(BH_3CH_3)_4 \cdot 2THF$ and $[U(BH_3CH_3)_4 \cdot THT]_2$.

Experimental

All preparations were carried out under an atmosphere of argon or under high vacuum. Toluene was dried over Na and distilled under argon before use. Diethyl ether and THF were distilled from sodium benzophenone ketyl under argon. Tetrahydrothiophene was dried over CaH_2 and distilled under argon before use. Benzene-d$_6$ and toluene-d$_8$ were degassed and dried over Na. Melting points (m.p.) were determined in sealed argon-filled capillaries and

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*Me = CH_3, Et = C_2H_5, Pr = C_3H_7, THF = OC_4H_8, THT = SC_4H_8.

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are uncorrected. $LiBH_3CH_3$ was prepared according to the procedure of Wartik and Schlesinger [7]. $U(BH_3CH_3)_4$ was prepared as described earlier [5a].

Preparation of *$U(BH_3CH_3)_4 \cdot 2THF$*

To 0.75 g (2.0 mmol) UCl_4 and 0.30 g (8.4 mmol) $LiBH_3CH_3$, about 5 ml of THF were added and stirred for 12 h. The THF was pumped off and the yellow–brown residue sublimed at 75 °C. A yield of 0.17 g (17%) of emerald green crystals was obtained. Its elemental analysis and ^1H NMR were consistent with the formula $U(BH_3CH_3)_4 \cdot 2THF$. Crystals suitable for X-ray crystallographic analysis were grown from a toluene solution at −20 °C. m.p. = 95–98 °C. *Anal.* Calc. for $C_{12}H_{40}B_4O_2U$: C, 28.96; H, 8.10. Found: C, 28.92; H, 7.87%.

Preparation of *$[U(BH_3CH_3)_4 \cdot THT]_2$*

$U(BH_3CH_3)_4$ (0.32 g, 0.91 mmol) was dissolved in toluene; 0.16 ml (1.8 mmol) THT was added and stirred for about 2 h; the solution was filtered, concentrated to 3 ml and cooled to −20 °C. Dark green crystals were obtained, which were washed with cold (−78 °C) hexene. A yield of 0.08 g (20%) was obtained. Its elemental analysis and ^1H NMR indicate it has the empirical formula, $U(BH_3CH_3)_4 \cdot THT$. m.p. = 92–94 °C. *Anal.* Calc. for $C_{16}H_{64}B_8S_2U_2$: C, 21.76; H, 7.30; S, 7.26. Found: C, 21.76; H, 7.17; S, 6.89%.

Infrared and ^1H NMR data are given in Tables I–III.

X-ray Diffraction

The air-sensitive crystals were sealed in quartz capillaries inside a dry box. A modified FACS-I Picker diffractometer was used to collect θ–2θ scanned single crystal X-ray diffraction data using graphite monochromated Mo Kα radiation. For the orthorhombic tetrahydrofuran structure a quadrant of data was collected to a 2θ angle of 60°; for the monoclinic thiophenate half a sphere of data was collected to a 2θ value of 50°. The data were corrected for absorption effects. The Friedel pairs in the non-centric orthorhombic structure were treated as independent reflections; the centric monoclinic equivalent reflections were averaged. Experimental details of the data collection and the results of the least-squares refinements are tabulated in the Supplementary Material. The structures were solved by Patterson and Fourier methods. The positional and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares. Hydrogen atoms were not included. Some of the difference Fourier peaks were identified as possible hydrogen atoms, but attempts to process them as hydrogen atoms in the least-squares refinements failed. The absolute configuration of the tetrahydrofuran complex was determined by comparing the results of the refinements of the enantiomorphic structure using *hkl* and $hk\bar{l}$ data (Friedel pairs); the structure reported here resulted in an *R* factor of 0.028 *versus* 0.032 for the inverted structure. Neutral atomic scattering factors were used [8] with the corrections for anomalous scattering applied. Positional parameters are given in Table IV. ORTEP structures are shown in Figs. 1 and 2 [9].

TABLE I. Infrared Spectroscopic Data

Compound				
$U(BH_3CH_3)_4 \cdot 2THF$				
2950m,	2230m,	2140s,	2080s,	1340m,
1300s,	1225s,	1100m,	1065m,	1040m,
1010s,	950m,	925m,	850s,	835m,
735m,	670m			
$[U(BH_3CH_3)_4 \cdot THT]_2$				
2950m,	2160s,	2080s,	1300s,	1240s,
1070m,	1030w,	960w,	890w,	800m,
725m,	665w			

TABLE II. Proton Magnetic Resonance Data[a]

Compound	
$U(BH_3CH_3)_4 \cdot 2THF$[b]	
+5.51 (8H, s),	+10.63 (12H, s)
+11.08 (8H, s),	+127.34 (12H, doub)
$[U(BH_3CH_3)_4 \cdot THT]_2$[c]	
+3.45 (8H, s),	+8.77 (8H, s)
+13.81 (24H, s),	+145.17 (24H, doub)

[a] Shifts in ppm from tetramethylsilane. Positive sign indicates downfield shift. All values at 30 °C. [b] Concentration = 1.2×10^{-3} g/ml benzene-d_6. [c] Concentration = 1.2×10^{-2} g/ml toluene-d_8.

TABLE III. ^1H NMR Data for $[U(BH_3CH_3)_4 \cdot THT]_2$[a,b,c]

T (°C)	BH_3	CH_3	THT
−90	−105.68 (12H, s)	−43.23 (12H, s)	−47.23 (8H, s)
	d	104.82 (12H, s)	−23.52 (8H, s)
−72	e	f	−30.75 (8H, s)
			−11.94 (8H, s)
−54	e	20.41 (24H, s)[g]	−10.79 (8H, s)
			−3.25 (8H, s)
30	145.17 (24H, s)[h]	13.81 (24H, s)[g]	3.45 (8H, s)
			8.77 (8H, s)

[a] In toluene-d_8. [b] Shifts in ppm from Me_4Si. Positive sign indicates downfield shift. [c] Concentration = 0.012 g/ml. [d] Other BH_3 peak too far downfield to be observed. [e] BH_3 broadened into baseline due to rapid exchange of BH_3CH_3 sites. [f] CH_3 peak broadened into baseline due to rapid exchange of BH_3CH_3 sites. [g] Averaged CH_3 peak. [h] Averaged BH_3 peak.

TABLE IV. Positional Parameters with Estimated Standard Deviations[a]

Atom	*x*	*y*	*z*
$(BH_3CH_3)_4U\cdot 2(OC_4H_8)$			
U	0.0	0.0	0.0
O	−0.1732(5)	0.0674(4)	−0.0070(22)
B(1)	0.0384(13)	0.1097(10)	−0.1800(17)
B(2)	0.0849(11)	0.0903(10)	0.1773(15)
C(1)	0.0739(10)	0.1738(9)	−0.2940(14)
C(2)	0.1287(10)	0.1504(9)	0.2945(15)
C(3)	−0.2699(10)	0.0277(9)	0.026(6)
C(4)	− 0.3554(9)	0.0915(11)	0.018(4)
C(5)	−0.3068(11)	0.1704(10)	0.015(5)
C(6)	−0.1922(11)	0.1544(8)	−0.023(5)
$[(CH_3BH_3)_4U\cdot SC_4H_8]_2$			
U(1)	0.21704(6)	0.20201(4)	−0.30664(4)
U(2)	0.27555(6)	−0.09460(4)	0.20013(4)
S(1)	0.3126(3)	0.10326(25)	0.19534(22)
S(2)	0.1840(3)	0.00630(28)	0.31517(23)
B(1)	0.1187(18)	0.1958(15)	0.4083(12)
B(2)	0.4320(15)	0.1723(11)	0.3856(11)
B(3)	0.2561(19)	0.3498(12)	0.2890(15)
B(4)	0.0398(17)	0.1933(13)	0.1876(12)
B(5)	0.0593(19)	−0.0632(14)	0.1264(13)
B(6)	0.4585(18)	−0.0821(13)	0.3205(12)
B(7)	0.2412(18)	−0.2406(13)	0.2185(14)
B(8)	0.3633(19)	−0.0935(13)	0.0944(14)
C(1)	0.0576(19)	0.1946(14)	0.4732(12)
C(2)	0.5670(15)	0.1593(12)	0.4342(11)
C(3)	0.2853(16)	0.4445(11)	0.2798(12)
C(4)	−0.0740(15)	0.1844(13)	0.1078(12)
C(5)	−0.0755(14)	−0.0427(12)	0.0826(11)
C(6)	0.5686(18)	−0.0786(12)	0.3957(12)
C(7)	0.2177(15)	−0.3373(12)	0.2252(13)
C(8)	0.4115(18)	−0.0980(12)	0.0230(12)
C(9)	0.4687(13)	0.1227(10)	0.2057(11)
C(10)	0.4670(19)	0.1660(17)	0.1324(13)
C(11)	0.3568(23)	0.1623(19)	0.0731(13)
C(12)	0.2513(15)	0.1381(12)	0.0956(9)
C(13)	0.0291(13)	−0.0181(11)	0.3090(10)
C(14)	0.0345(19)	−0.0569(18)	0.3823(14)
C(15)	0.1433(23)	−0.0566(20)	0.4386(15)
C(16)	0.2479(16)	−0.0280(12)	0.4165(9)

[a]Estimated standard deviations in this and subsequent tables are indicated in parentheses.

Discussion

The crystal structure of $U(BH_3CH_3)_4\cdot 2THF$ is very similar to that of $U(BH_4)_4\cdot 2THF$ [2b]. The four BH_3CH_3 groups and two THF groups form a distorted octahedron about the uranium (Fig. 1). The THF groups are *trans* to each other. The U–B–C angles are close to 180°, indicative of tridentate ligation to the metal. The average U–B distance (2.57 ± 0.02 Å) compares favorably with the tridentate U–B distance found in $U(BH_4)_4\cdot 2THF$ (2.56(4) Å) [2b]. It is larger than that found for $U(BH_3CH_3)_4$ (2.48 ± 0.03 Å) [5a], presumably due to its larger coordination number (14 *vs.* 12). The U–O bond distance (2.485(6) Å) is also close to that of $U(BH_4)_4\cdot 2THF$ (2.47(1) Å) [2b]. Selected bond distances and angles are given in Table V.

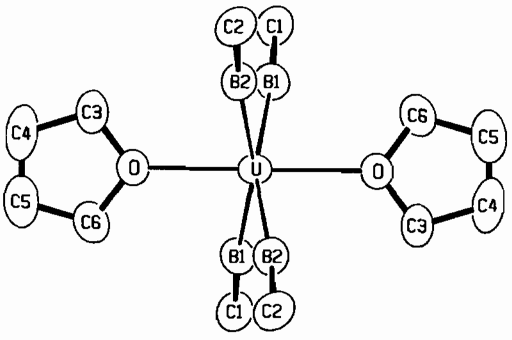

Fig. 1. ORTEP drawing of $U(BH_3CH_3)_4\cdot 2(OC_4H_8)$; thermal ellipsoids at 50% probability level.

The crystal structure shows that $[U(BH_3CH_3)_4\cdot THT]_2$ is dimeric, but with a different structure than $[Th(BH_3CH_3)_4\cdot THF]_2$ [5c]. The two U atoms are bridged by the sulfur atoms of the THT groups (see Fig. 2). The plane of the two bridging THT groups is perpendicular to the plane containing the U(1), U(2), S(1), S(2) atoms. Selected bond distances and angles are given in Table V. All of the BH_3CH_3 groups are tridentate. The average U–B distance is 2.54 ± 0.04 Å, which is comparable with the average U–B(tridentate) bond length of 2.57 ± 0.04 Å found in $U(BH_3CH_3)_4\cdot 2THF$. The two average U–S bond lengths are 3.14 ± 0.03 and 3.26 ± 0.03 Å. There are two different BH_3CH_3 sites of equal population, those that are pointed towards the THT groups and those that are pointed away from them. These two different sites are observed in the ^1H NMR spectrum. IR and ^1H NMR spectral data are presented in Tables I–III. In the ^1H NMR spectrum of $[U(BH_3CH_3)_4\cdot THT]_2$, we see one BH_3CH_3 site, which coalesces and then splits into two different BH_3CH_3 sites of equal population at −90 °C (see Table III). The mono-THT adduct of $U(BH_3CH_3)_4$ is probably not a monomer in solution like $U(BH_3CH_3)_4\cdot THF$, since equivalent BH_3CH_3 sites were observed in the NMR spectrum at low temperatures for the latter [5c].

Geometric calculations using the cone angle model of Bagnall and Li [10] do not indicate any major steric factors in the coordination geometry of the $[U(BH_3CH_3)\cdot THT]_2$ complex with bridging THT groups or an assumed structure based on the geometry of $[Th(BH_3CH_3)_4\cdot THF]_2$ with bridging methyltrihydroborate groups. Thus electronic effects may be the reason for the preferred dimeric geometry in $[U(BH_3CH_3)\cdot THT]_2$.

Comparison of the Lewis base adducts $Th(BH_3CH_3)_4$ and $U(BH_3CH_3)_4$ is instructive. The Th(IV)

TABLE V. Selected Bond Distances and Angles

$(BH_3CH_3)_4U\cdot 2(OC_4H_8)$[a]		$[(CH_3BH_3)_4U\cdot SC_4H_8]_2$			
Distances (Å)					
U–B(1)	2.583(17)	U(1)–B(1)	2.533(17)	U(2)–B(5)	2.574(22)
		U(1)–B(2)	2.578(18)	U(2)–B(6)	2.591(22)
U–B(2)	2.554(15)	U(1)–B(3)	2.506(20)	U(2)–B(7)	2.468(21)
		U(1)–B(4)	2.532(22)	U(2)–B(8)	2.511(20)
U–O	2.485(6)	U(1)–S(1)	3.120(4)	U(2)–S(1)	3.275(4)
		U(1)–S(2)	3.239(5)	U(2)–S(2)	3.165(4)
B(1)–C(1)	1.613(21)	B(1)–C(1)	1.600(22)	B(5)–C(5)	1.601(26)
B(2)–C(2)	1.630(19)	B(2)–C(2)	1.600(23)	B(6)–C(6)	1.585(27)
		B(3)–C(3)	1.611(24)	B(7)–C(7)	1.621(27)
		B(4)–C(4)	1.669(28)	B(8)–C(8)	1.610(25)
		S(1)–S(2)	3.477(5)	U(1)–U(2)	5.374(1)
Angles (°)					
O–U–O	176.7(10)	S(1)–U(1)–S(2)	66.3(1)	S(1)–U(2)–S(2)	65.3(1)
O–U–B(1)	81.6(5)	S(1)–U(1)–B(1)	146.4(6)	S(1)–U(2)–B(5)	84.9(5)
O–U–B(1)	96.0(5)	S(1)–U(1)–B(2)	76.1(4)	S(1)–U(2)–B(6)	81.9(5)
O–U–B(2)	99.1(5)	S(1)–U(1)–B(3)	106.8(5)	S(1)–U(2)–B(7)	172.7(6)
O–U–B(2)	83.2(5)	S(1)–U(1)–B(4)	77.4(4)	S(1)–U(2)–B(8)	82.9(5)
B(1)–U–B(1)′	90.3(8)	S(2)–U(1)–B(1)	80.2(6)	S(2)–U(2)–B(5)	74.9(5)
B(1)–U–B(2)	91.4(4)	S(2)–U(1)–B(2)	84.4(4)	S(2)–U(2)–B(6)	76.3(5)
B(1)–U–B(2)′	164.9(4)	S(2)–U(1)–B(3)	173.0(5)	S(2)–U(2)–B(7)	107.6(6)
B(2)–U–B(2)′	90.8(7)	S(2)–U(1)–B(4)	84.5(5)	S(2)–U(2)–B(8)	148.1(5)
U–B(1)–C(1)	174.0(11)	B(1)–U(1)–B(2)	101.3(7)	B(5)–U(2)–B(6)	151.2(6)
O–B(1)–C(1)	138.0(10)	B(1)–U(1)–B(3)	106.8(8)	B(5)–U(2)–B(7)	94.6(7)
U–B(2)–C(2)	174.9(11)	B(1)–U(1)–B(4)	100.4(7)	B(5)–U(2)–B(8)	101.2(7)
O–B(2)–C(2)	137.4(11)	B(2)–U(1)–B(3)	93.4(7)	B(6)–U(2)–B(7)	95.3(7)
		B(2)–U(1)–B(4)	153.5(6)	B(6)–U(2)–B(8)	102.5(7)
		B(3)–U(1)–B(4)	94.7(8)	B(7)–U(2)–B(8)	104.3(7)
		U(1)–S(1)–U(2)	114.3(1)	U(1)–S(2)–U(2)	114.09(1)
		U(1)–B(1)–C(1)	178.3(16)	U(2)–B(5)–C(5)	178.5(14)
		U(1)–B(2)–C(2)	176.7(13)	U(2)–B(6)–C(6)	177.1(14)
		U(1)–B(3)–C(3)	178.1(17)	U(2)–B(7)–C(7)	176.5(18)
		U(1)–B(4)–C(4)	177.5(14)	U(2)–B(8)–C(8)	175.4(15)

[a] Primed atoms are in position $-x$, $-y$, z.

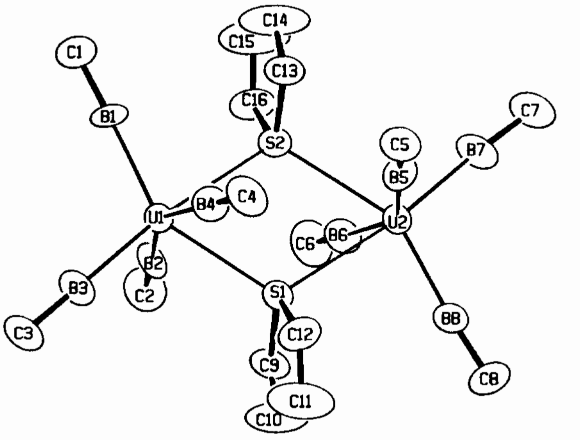

Fig. 2. ORTEP drawing of $[(CH_3BH_3)_4U\cdot S_4H_8]$; thermal ellipsoids at 50% probability level.

ion appears to require a larger coordination number which results in the formation of the unusual dimers $[Th(BH_3CH_3)_4]_2\cdot OEt_2$ and $[Th(BH_3CH_3)_4]_2\cdot 2THF$. The analogous $U(BH_3CH_3)_4$ compounds have not been isolated. $Th(BH_3CH_3)_4$ forms a bis-THF complex, a bis-THT complex and a mono-THT complex. On the other hand, we have only been able to isolate for $U(BH_3CH_3)_4$ the bis-THF complex and the dimeric-THT complex, $[U(BH_3CH_3)_4\cdot THT]_2$. Clearly, the larger ionic radius of Th(IV) plays a major role in the unusual coordination chemistry of ether adducts of $Th(BH_3CH_3)_4$.

Supplementary Material

Listings of thermal parameters, additional distances and angles, and observed structure factors have been deposited with the Editor-in-Chief.

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