Tetrahydroborate Complexes of Uranium: Preparation and Crystal Structure of Mixed-valent $[Na(THF)_6][(C_5Me_5)U(BH_4)_3]_2$

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Abstract

Reaction of $U(BH_4)_3 \cdot n$THF with $Cp^*{}_2Th(PPh_2)_2$ in a THF/toluene solution containing NaCl resulted in isolation of the novel tetrahydroborate complex $[Na(THF)_6][Cp^*U(BH_4)_3]_2$, $Cp^* = C_5Me_5$. The complex crystallizes in the space group $P1$ with cell parameters of $a = 11.110(3)$, $b = 15.140(3)$, $c = 17.856(3)$ Å, $\alpha = 88.27(1)$, $\beta = 74.49(2)$ and $\gamma = 85.42(2)°$, $Z = 2$ and $D_{calc} = 1.49$ g/cm^3. The unit cell contains two crystallographically independent uranium atoms in general positions, each coordinated by three tridentate, hydrogen-bridged BH_4^- groups and one η^5-pentamethylcyclopentadienyl ligand. Two $Na(THF)_6^+$ cations, which occupy centers of crystallographic symmetry, complete the structure. Metrical parameters are not significantly different between the two independent uranium centers (av. U–B distances 2.61 Å) or the two independent sodium containing cations. Crystallographically independent $Cp^*U(BH_4)_3$ moieties pack to form two separate chains parallel to the crystallographic *a* axis. The stoichiometry and accompanying black color for the crystal suggest a mixed-valent charge transfer compound for which the average uranium oxidation state is 3.5. An unexpected Cp* transfer from thorium to uranium is also noted in the reaction chemistry.

Introduction

We recently reported the synthesis and characterization of the thorium(IV) bis(diphenylphosphide) complex, $Cp^*{}_2Th(PPh_2)_2$ [1]. Subsequent reactions to form the first transition metal–actinide heterobimetallic complexes $Cp^*{}_2Th(\mu\text{-}PPh_2)_2Ni(CO)_2$ [2a] and $Cp^*{}_2Th(\mu\text{-}PPh_2)_2Pt(PMe_3)$ [2b] have also been reported. The former complex showed clear indications of Th–Ni bonding, while the Th–Pt distance in the latter system was indicative of a single metal–metal bond. Previous investigations of the chemistry of $U(BH_4)_3 \cdot n$THF have produced complexes of the type $U(BH_4)_3 \cdot 2L$ [3], where L = 2-(diphenylphosphino)pyridine or 1,2-bis(dimethylphosphino)ethane (dmpe). The structure of a related complex, $U(BH_3Me)_3(dmpe)_2$, has also been reported [4]. Because $Cp^*{}_2Th(PPh_2)_2$ exhibits chemistry which, in some cases, is similar to that of bidentate phosphines, an extension to complexes of the type $U(BH_4)_3 \cdot 2L$ where $L = Cp^*{}_2Th(PPh_2)_2$ seemed reasonable.

Herein we describe the reaction between $Cp^*{}_2Th(PPh_2)_2$ and $U(BH_4)_3 \cdot n$THF and its surprising result.

Experimental

General Information

Manipulations of air-sensitive solids and solutions were performed either under argon using Schlenk techniques, or within the confines of a helium-filled Vacuum Atmospheres glovebox, equipped with a high capacity (MO-40-2H) Dri-Train purification system. Uranium tetrachloride was prepared from UO_3 and hexachloropropene [5].

$U(BH_4)_3 \cdot n$THF

$UCl_3(THF)_x$ [6] and subsequently $U(BH_4)_3 \cdot n$THF were prepared by condensing 70 ml dry, degassed THF onto a mixture of 0.38 g (1 mmol) UCl_4 and 0.24 g (10 mmol) NaH and stirring for 4.5 h at room temperature (RT). The resulting purple solution was filtered (fine frit) onto 0.12 g (3 mmol) $NaBH_4$, stirred overnight at RT, refiltered, yielding a red solution of the soluble uranium(III) BH_4^- complex.

$ThCp^*{}_2(PPh_2)_2$

A total of 0.574 g (1 mmol) $ThCp^*{}_2Cl_2$ and 0.576 g (3 mmol) $LiPPh_2$ was placed in 50 ml anhydrous toluene, stirred overnight, filtered, producing a purple solution of the Th(IV) complex.

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*[Na(THF)$_6$][Cp*U(BH$_4$)$_3$]$_2$*

The $Cp^*_2Th(PPh_2)_2$ solution (toluene) was slowly added to the $U(BH_4)_3 \cdot n$THF solution (THF) and stirred at room temperature for 1 h. The resulting green solution was reduced in volume (*in vacuo*) to remove THF in anticipation of preparing the desired heterobimetallic product. A dark solid separated from the solution. Following collection on a fine frit, it was recrystallized from a toluene/hexane mixture (ice bath), yielding black crystals which were identified via X-ray crystallography as described below.

Crystal Data and Structure Determination

Room temperature data were collected by variable speed θ–2θ scans on an Enraf Nonius CAD-4 diffractometer equipped with a graphite monochromator and using Mo Kα radiation. The structure was solved using standard Patterson and difference Fourier methods and refined to the observed data ($I \geqslant 2\sigma(I)$) with full-matrix least-squares methods using appropriate neutral scattering factors and anomalous scattering terms [7]. The correct formula was shown to be $[Na(THF)_6][Cp^*U(BH_4)_3]_2$. Refinements included anisotropic thermal parameters for uranium and sodium plus a correction for secondary extinction [8]. Final Fourier difference maps failed to show peaks which could be interpreted as hydrogen atoms. The Los Alamos Crystal Structure Codes [9] were used for all calculations. Data were corrected for absorption using the relative intensity of a low angle reflection measured as a function of Ψ (mapped to ϕ) multiplied by a spherical correction using a radius calculated from the average distance between the three most prominent directions of crystal development. The function minimized was $R_F = \Sigma w^2 [F_o - F_c]^2$ and weights were calculated as $w^2 = 4F^2/\sigma^2(I)$ where $\sigma(I) = \sigma_C(I) + (0.030 \times I)^2$; $\sigma_C(I)$ is the error based on counting statistics. Lattice and data collection parameters are given in Table 1. Fractional coordinates and bond distances and angles are given in Tables 2 and 3, respectively. ORTEP projections with appropriate numbering schemes for the two crystallographically distinct uranium-containing moieties are shown in Fig. 1.

TABLE 1. X-ray data for $[Na(THF)_6][(C_5Me_5)U(BH_4)_3]_2$

Formula	$C_{44}H_{102}B_6O_6NaU_2$
Color	black
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	11.110(3)
b (Å)	15.140(3)
c (Å)	17.856(3)
α (°)	88.27(1)
β (°)	74.49(2)
γ (°)	85.42(2)
V (Å^3)	2884.5
Z	2
D_{calc} (g cm^{-3})	1.49
λ(Mo Kα1)	0.70930
Temperature (°C)	23
Crystal dimensions (mm)	0.2 × 0.2 × 0.3
Absorption coefficient (cm^{-1})	53.6
Absorption correction type	ϕ × sphere
Sphere radius (mm)	0.2
Transmission (min., max.)	0.31, 0.49
Ave. peak width (w) (°)	0.7
Scan type	θ–2θ
Scan range (°)	$0 \leqslant 2\theta \leqslant 45°$ ($h, \pm k, \pm l$)
Scan rate	variable
No. reflections	8448
No. unique reflections	7508
No. with $I \geqslant 2\sigma(I)$	4742
R_F equiv. reflections (%)	1.4
R_F observed reflections (%)	4.2
R_{wF} observed reflections (%)	5.5

Results and Discussion

The unit cell contains two crystallographically independent uranium atoms in general positions, each

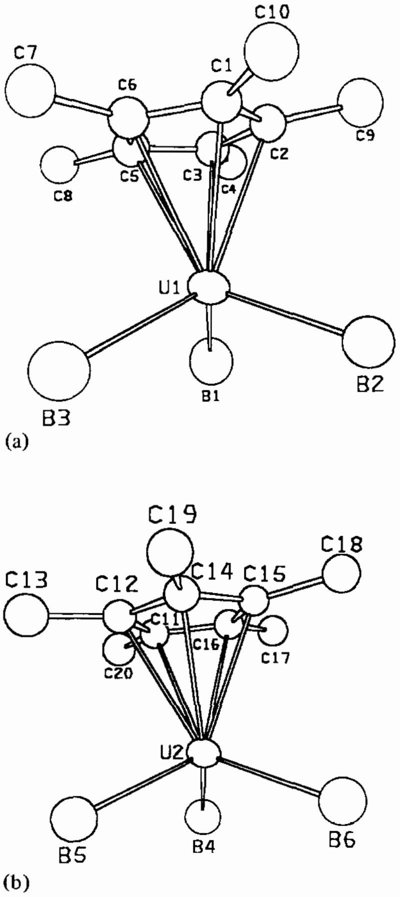

Fig. 1. ORTEP projections for the two crystallographically independent uranium-containing anions.

TABLE 2. Fractional coordinates and equivalent isotropic thermal parameters for $[Na(THF)_6][(C_5Me_5)U(BH_4)_3]_2$

Atom	x	y	z	B	Atom	x	y	z	B
U(1)	0.14258(5)	0.00916(4)	0.20055(3)	5.88[a]	U(2)	0.19093(5)	0.46199(4)	0.68481(3)	5.00[a]
Na(1)	0.5000(0)	0.0000(0)	0.5000(0)	4.0[a]	Na(2)	0.5000(0)	0.5000(0)	0.0000(0)	4.0[a]
B(1)	−0.044(2)	0.102(2)	0.166(1)	8.4(6)	B(2)	0.061(2)	−0.019(1)	0.348(1)	6.6(5)
B(3)	0.319(2)	0.124(2)	0.181(1)	8.6(6)	C(1)	0.266(1)	−0.156(1)	0.171(1)	4.4(3)
C(2)	0.142(1)	−0.166(1)	0.168(1)	4.4(3)	C(3)	0.119(1)	−0.121(1)	0.103(1)	4.5(3)
C(4)	0.003(1)	−0.121(1)	0.073(1)	5.6(4)	C(5)	0.232(1)	−0.081(1)	0.063(1)	4.9(3)
C(6)	0.323(1)	−0.105(1)	0.107(1)	4.7(3)	C(7)	0.461(2)	−0.085(1)	0.079(1)	6.4(4)
C(8)	0.255(1)	−0.027(1)	−0.012(1)	5.7(4)	C(9)	0.052(2)	−0.230(1)	0.221(1)	6.7(4)
C(10)	0.332(1)	−0.199(1)	0.231(1)	5.7(4)	B(4)	0.085(2)	0.352(1)	0.620(1)	7.1(5)
B(5)	0.070(2)	0.465(1)	0.833(1)	6.5(5)	B(6)	0.409(2)	0.383(1)	0.680(1)	7.7(6)
C(11)	0.096(1)	0.602(1)	0.611(1)	3.9(3)	C(12)	0.106(1)	0.637(1)	0.682(1)	4.3(3)
C(13)	−0.006(2)	0.674(1)	0.747(1)	6.9(4)	C(14)	0.233(1)	0.638(1)	0.677(1)	4.4(3)
C(15)	0.305(1)	0.603(1)	0.605(1)	3.6(3)	C(16)	0.217(1)	0.581(1)	0.564(1)	4.0(3)
C(17)	0.249(1)	0.549(1)	0.479(1)	4.9(3)	C(18)	0.447(1)	0.600(1)	0.572(1)	5.1(3)
C(19)	0.286(1)	0.678(1)	0.739(1)	5.6(4)	C(20)	−0.025(1)	0.595(1)	0.586(1)	5.8(4)
O(1)	0.3761(9)	1.1003(6)	0.4714(5)	5.1(2)	C(21)	0.248(2)	1.086(1)	0.464(1)	7.7(5)
C(22)	0.199(2)	1.179(1)	0.440(1)	8.9(5)	C(23)	0.309(2)	1.235(1)	0.413(1)	9.0(5)
C(24)	0.404(2)	1.194(1)	0.455(1)	6.8(4)	O(2)	0.5793(9)	0.9727(6)	0.3801(5)	5.1(2)
C(25)	0.544(2)	1.027(1)	0.317(1)	6.9(4)	C(26)	0.629(2)	0.980(1)	0.247(1)	10.2(6)
C(27)	0.677(2)	0.892(1)	0.263(1)	10.2(6)	C(28)	0.677(2)	0.901(1)	0.347(1)	8.3(5)
O(3)	0.3691(8)	0.9047(6)	0.5039(5)	4.7(2)	C(29)	0.360(1)	0.853(1)	0.437(1)	5.9(4)
C(30)	0.252(2)	0.795(1)	0.467(1)	7.8(5)	C(31)	0.174(2)	0.832(1)	0.541(1)	7.0(4)
C(32)	0.267(2)	0.882(1)	0.576(1)	6.5(4)	O(4)	0.4175(9)	0.5021(6)	0.1204(5)	4.8(2)
C(33)	0.460(1)	0.443(1)	0.179(1)	5.3(3)	C(34)	0.349(2)	0.448(1)	0.250(1)	7.1(4)
C(35)	0.288(2)	0.541(1)	0.248(1)	7.5(4)	C(36)	0.304(2)	0.560(1)	0.161(1)	6.1(4)
O(5)	0.6191(8)	0.6006(6)	0.0094(5)	4.6(2)	C(37)	0.714(1)	0.638(1)	−0.054(1)	5.8(4)
C(38)	0.797(2)	0.686(1)	−0.016(1)	10.2(6)	C(39)	0.718(2)	0.706(1)	0.062(1)	9.2(5)
C(40)	0.618(2)	0.642(1)	0.083(1)	6.6(4)	O(6)	0.6357(8)	0.4021(6)	0.0150(5)	4.6(2)
C(41)	0.624(1)	0.308(1)	0.016(1)	5.6(4)	C(42)	0.723(1)	0.270(1)	0.056(1)	5.8(4)
C(43)	0.825(2)	0.331(1)	0.030(1)	6.6(4)	C(44)	0.757(1)	0.422(1)	0.030(1)	5.7(4)

[a] $[(U_{11} + U_{22} + U_{33})/3] \times 100$.

TABLE 3. Selected distances (Å) and angles (°) for $[Na(THF)_6][(C_5Me_5)U(BH_4)_3]_2$

U1–B1	2.61(2)	U2–B4	2.58(2)
U1–B2	2.57(2)	U2–B5	2.64(2)
U1–B3	2.68(2)	U2–B6	2.59(2)
U1–C1	2.75(1)	U2–C11	2.75(1)
U1–C2	2.74(1)	U2–C12	2.75(1)
U1–C3	2.74(1)	U2–C14	2.74(1)
U1–C5	2.75(1)	U2–C15	2.74(1)
U1–C6	2.76(1)	U2–C16	2.75(1)
C1–C2	1.41(2)	C11–C12	1.42(2)
C1–C10	1.55(2)	C11–C20	1.54(2)
C2–C3	1.40(2)	C12–C14	1.39(2)
C2–C9	1.56(2)	C12–C13	1.53(2)
C3–C5	1.43(2)	C14–C15	1.41(2)
C3–C4	1.52(2)	C14–C19	1.55(2)
C5–C6	1.45(2)	C15–C16	1.43(2)
C5–C8	1.52(2)	C15–C18	1.52(2)
C6–C1	1.40(2)	C16–C11	1.41(2)
C6–C7	1.54(2)	C16–C17	1.54(2)
B1–U1–B2	103.2(7)	B4–U2–B5	106.7(6)
B1–U1–B3	103.6(7)	B4–U2–B6	104.4(7)
B2–U1–B3	107.3(7)	B5–U2–B6	104.7(6)
Na1–O1	2.11(1)	Na2–O4	2.10(1)
Na1–O2	2.13(1)	Na2–O5	2.13(1)
Na1–O3	2.12(1)	Na2–O6	2.09(1)
O1–Na1–O2	89.7(4)	O4–Na2–O5	91.2(3)
O1–Na1–O3	89.4(4)	O4–Na2–O6	90.5(3)
O2–Na1–O3	89.3(3)	O5–Na2–O6	90.3(3)

coordinated by three tridentate, hydrogen-bridged BH_4^- groups and one η^5-pentamethylcyclopentadienyl ligand. Two $Na(THF)_6^+$ cations, on centers of crystallographic symmetry, complete the structure. Metrical parameters are not significantly different for the two independent uranium centers (av. U–B distances 2.61 Å). Each of the two crystallographically independent $Cp^*U(BH_4)_3$ moieties are related, across a center of symmetry, in a head-to-tail fashion to form pairs which are translationally related within chains parallel to the *a* axis. These two chains, comprised of crystallographically distinct, but metrically similar, $Cp^*U(BH_4)_3$ units, are separated from each other by columns of $Na(THF)_6^+$. Between the chains there are two U(1)–U(2) distances, viz. 8.25 and 8.61 Å. Within one chain the two U(1) distances are 8.59 and 9.15 Å; within the other the U(2)–U(2) distances are 8.28 and 8.75 Å. The stoichiometry and accompanying black color for the crystal suggest a mixed valent charge transfer complex for which the average uranium oxidation state is 3.5.

Several cyclopentadienyl tetrahydroborate complexes of U(IV) have been prepared and structurally characterized. For example, the series $(C_5H_5)U(BH_4)_3$ [10a], $(C_5H_5)_2U(BH_4)_2$ [10b], and $(C_5H_5)_3U(BH_4)$ [10c] has been synthesized using various metathetical approaches. Tetrahydroborate complexes of U(III) are less well known [3, 4] and Cp and Cp* ligated uranium(III) borohydride complexes have not been reported.

Although the hydrogen atoms of the BH_4^- groups were not located, the BH_4^- ligands are likely tridentate providing a uranium coordination number of 12, a reasonable environment for both U(III) and U(IV) complexes of this type. The U–B distances reported herein (2.61 Å ave.) are well within the range identified [11] as being characteristic of tridentate BH_4^- groups for U(IV), e.g. 2.61 Å for $Cp_2U(BH_4)_2$ [10b] and 2.56 Å for $U(BH_4)_4(THF)$ [12]. Edelstein *et al.* [4] have recently reported similar U–BH_4 tridentate distances for tetravalent and trivalent uranium methyltrihydroborates, i.e. 2.57 Å and 2.64 Å for $U(BH_3CH_3)_4(dmpe)$ and $U(BH_3CH_3)_3(dmpe)_2$, respectively. In comparison, U–B distances of 2.8–2.88 Å have been observed for bidentate coordination of borohydride to U(IV) [3, 11, 12].

The average U–C distance for $[Na(THF)_6][Cp^*U(BH_4)_3]_2$ is 2.74 Å. This value is larger than the mean U–C distance of 2.64 Å observed for $CpU(BH_4)_3$ [10a], but somewhat smaller than one would estimate for the isostructural anion based on a value of 0.14 Å for Δr[U(III)–U(IV)]. The value for Δr was determined from the estimated ionic radius for U(III) in $Cp_3U(THF)$ [13] and the 1.06 Å U(IV) radius estimated by Raymond and Eigenbrot [14] for ten coordinate U(IV) complexes. The present result is consistent with an oxidation state intermediate between 3 and 4; presumably 3.5 from the crystallographically determined formula. The intense black color is, no doubt, due to a low energy and, therefore, facile U(III) → U(IV) charge transfer process, resulting in the two metrically equivalent but cyrstallographically distinct $Cp^*U(BH_4)_3$ moieties observed here.

An unexpected feature associated with the formation of the title compound is the migration of a Cp* from thorium to the uranium center. There is no precedent for such a transfer. Ostensibly, the other main reaction product could be $Cp^*Th(PPh_2)_2Cl$. The sodium source was presumably NaCl which was carried along through the filtration steps. Moody *et al.* [15] have noted only a 50–60% removal of NaCl when sodium phenoxide was added to a THF solution of $UCl_3(THF)_x$. This tendency to carry along NaCl was not eliminated, though of course lessened by removal of THF and utilization of the noncoordinating solvent toluene.

Rational synthesis of $[Na(THF)_6][Cp^*U(BH_4)_3]$ has been attempted by two alternate approaches. $Cp^*UCl_3(THF)_2$ [16] was reacted with 3 equivalents of $NaBH_4$ in THF to yield $Cp^*U(BH_4)_3$, followed by sodium amalgam reduction. A second approach involved direct reaction of $U(BH_4)_3 \cdot n$THF with one equivalent of NaCp* in THF. In both cases red products resulted which were clearly not the target compound.

Supplementary Material

Tables of anisotropic thermal parameters and observed and calculated structure factors can be obtained from the corresponding author upon request.

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