

**(18-Crown-6)- $\mu$ -oxo-hexakis(tetrahydroborato)diuranium(IV): an unprecedented asymmetric dinuclear complex**

Claude Villiers, Pierre Thuéry\* and Michel Ephritikhine

CEA/Saclay, DSM/DRECAM/SCM (CNRS URA 331), Bâtiment 125, 91191 Gif-sur-Yvette, France

Correspondence e-mail: pierre.thuery@cea.fr

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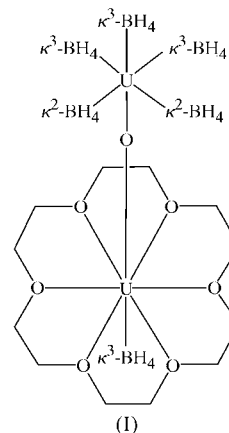
In the title compound, (1,4,7,10,13,16-hexaoxacyclooctadecane-1 $\kappa^6$ O)- $\mu$ -oxo-1:2 $\kappa^2$ O:O-hexakis(tetrahydroborato)-1 $\kappa^3$ H;-2 $\kappa^2$ H;2 $\kappa^2$ H;2 $\kappa^3$ H;2 $\kappa^3$ H;2 $\kappa^3$ H-diuranium(IV), [U<sub>2</sub>(BH<sub>4</sub>)<sub>6</sub>O(C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>)], one of the U atoms (U1), located at the centre of the crown ether moiety, is bound to the six ether O atoms, and also to a tridentate tetrahydroborate group and a  $\mu$ -oxo atom in axial positions. The other U atom (U2) is bound to the same oxo group and to five tetrahydroborate moieties, three of them tridentate and the other two bidentate. The two metal centres are bridged by the  $\mu$ -oxo atom in an asymmetric fashion, thus giving the species (18-crown-6)( $\kappa^3$ -BH<sub>4</sub>)U=( $\mu$ -O)-U( $\kappa^3$ -BH<sub>4</sub>)<sub>3</sub>( $\kappa^2$ -BH<sub>4</sub>)<sub>2</sub>, in which the U1=O and U2-O bond lengths to the  $\mu$ -O atom [1.979 (5) and 2.187 (5) Å, respectively] are indicative of the presence of positive and negative partial charges on U1 and U2, respectively.

**Comment**

Examples of hexa-coordinated (18-crown-6)uranium complexes are uncommon. The first to be reported were uranium(IV) complexes, in which the coordination sphere was completed by three chloride groups (de Villardi *et al.*, 1978; Bombieri *et al.*, 1978). A bis(tetrahydroborate) uranium(III) complex with dicyclohexyl-18-crown-6 has also been described (Dejean *et al.*, 1987), as well as several uranyl complexes (Thuéry *et al.*, 1995, and references therein). In the course of our studies of the reactions of tetramethylethylene with U(BH<sub>4</sub>)<sub>4</sub> (Villiers & Ephritikhine, 1995), we obtained the title compound, (I), which appeared to be a dinuclear molecular complex of unprecedented geometry.

The asymmetric unit of (I) comprises one complex molecule (Fig. 1). The two U centres are bridged by the  $\mu$ -oxo atom O7 in an asymmetric fashion, this atom being closer to U1 than to U2 by *ca* 0.21 Å, the ensemble being close to linearity [U1-O7-U2 = 173.8 (3)°]. A search of the Cambridge Structural Database (CSD; Version 5.27; Allen, 2002) shows that quasi-

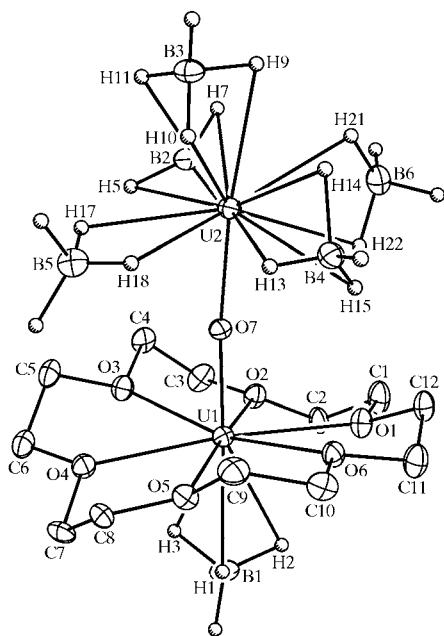
linear  $\mu_2$ -oxo-diuranium systems are generally symmetrical, with U-O bond lengths in the range 2.06–2.11 Å and the two U atoms in similar environments. Only one example of a system in which the bridge is nearly perfectly linear and the two bond lengths different (2.017 and 2.226 Å) has been described, but it is a mixed-valence U<sup>III</sup>/U<sup>IV</sup> species (Korobkov *et al.*, 2002). This asymmetry in the U-O bond lengths in (I) is probably indicative of a U1=O7-U2 bonding scheme, associated with positive and negative partial charges on U1 and U2, respectively.



Atom U1 is located at the centre of the 18-crown-6 molecule, in which it is held by six bonds to the ether O atoms. The U-O(ether) bond lengths are in the range 2.517 (6)–2.581 (6) Å and their average value of 2.55 (2) Å is in good agreement with the values of 2.55 (9) (de Villardi *et al.*, 1978) and 2.53 (5) Å (Bombieri *et al.*, 1978) in similar systems. The six ether O atoms define a mean plane with an r.m.s. deviation of 0.22 Å, atom U1 being 0.014 (2) Å from this plane. The O-C-C-O torsion angles are all *gauche* [in the range 47.2 (9)–53.5 (9)°] and define a  $g^+g^-g^+g^-g^+g^-$  sequence (distorted  $D_{3d}$  symmetry), which is commonly found in uncomplexed as well as complexed crown ethers (Fyles & Gandour, 1992). However, some C-O-C-C torsion angles deviate by as much as *ca* 37° from the ideal *anti* value [143.3 (7)–176.5 (7)°]. Oxo atom O7 and the tetrahydroborate group are located on either side of the crown ether mean plane and are axially bound to U1 [O7-U1...B1 = 178.0 (3)°]. The BH<sub>4</sub> group is tridentate, with U1-H bond lengths in the range 2.35–2.48 Å [mean value = 2.40 (5) Å] and B-H bond lengths in the range 1.12–1.21 Å [mean value = 1.16 (4) Å]. It has been shown that the U...B distance in uranium tetrahydroborates is indicative of the nature (bi- or tridentate) of the bonding (Bernstein *et al.*, 1972; Edelstein, 1981). The U1...B1 distance of 2.617 (10) Å in (I) agrees with the average distance for tridentate ligands from the CSD, 2.58 (6) Å (7 hits). If the BH<sub>4</sub> group is considered as a single donor atom, the uranium environment is a very distorted hexagonal bipyramid.

The second metal centre, U2, is bound to the bridging atom O7 and to five tetrahydroborate groups, among which three are tridentate (B2, B3 and B4) and two bidentate (B5 and B6). The tridentate ligands correspond to U2-H bond lengths in

the range 2.21–2.69 Å [mean value = 2.49 (15) Å], B–H bond lengths in the range 1.01–1.39 Å [mean value = 1.17 (13) Å] and U2···B distances in the range 2.595 (10)–2.652 (11) Å [mean value = 2.63 (2) Å]. These three groups are thus slightly farther from U2 than their counterpart is from U1, maybe as a result of the crowding around U2. For the two bidentate ligands, the U2–H bond lengths are in the range 2.36–2.70 Å [mean value = 2.50 (13) Å], the B–H bond lengths are in the range 0.94–1.28 Å [mean value = 1.13 (10) Å] and the U2···B distances are 2.918 (11) and 2.921 (11) Å, these last unambiguously evidencing the coordination mode. Indeed, there are only three well documented examples (*i.e.* with H atoms located, albeit with moderate reliability in certain cases) of bidentate tetrahydroborate complexes of U<sup>IV</sup> in the CSD (Bernstein *et al.*, 1972; Rietz *et al.*, 1978; Charpin *et al.*, 1987), with an average U···B distance of 2.87 (3) Å [the mean U–H and B–H bond lengths are 2.38 (15) and 1.24 (8) Å, respectively]. In (I), the tetrahydroborate group in the *trans* position with respect to O7 is tridentate, the two bidentate groups being *trans* to each other. The four atoms B2, B4, B5 and B6 define a plane, with an r.m.s. deviation of 0.079 Å, which is nearly parallel to the mean plane defined by the six O atoms of the crown ether, with a dihedral angle of 8.7 (3)°. Atom U2 is only 0.133 (5) Å from this mean plane, with atoms O7 and B3 occupying the axial positions [O7–U2···B3 = 158.7 (3)°], the metal environment being thus distorted octahedral, if the tetrahydroborate groups are considered as single donor atoms. Surprisingly, one of the bidentate groups (B5) has the bite angle defined by the two coordinating H atoms roughly parallel to the mean B<sub>4</sub> plane, whereas the other group (B6) is roughly perpendicular to it [dihedral angles between the BH<sub>2</sub>



**Figure 1**

A view of compound (I), showing the atom-numbering scheme. The H atoms of the crown ether have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

and mean B<sub>4</sub> planes of 9.8 (3) and 89.34 (12)°, respectively]. As a consequence, the B···U2···B angles involving successive B atoms in the B<sub>4</sub> plane are much larger around B5 [B2···U2···B5 = 100.4 (3)° and B4···U2···B5 = 100.1 (3)°] than around B6 [B2···U2···B6 = 79.6 (3)° and B4···U2···B6 = 79.6 (3)°]. This may also be the reason why the O7–U2···B3 angle deviates from linearity, the B3···U2···B5 angle [82.5 (3)°] being smaller than the B3···U2···B6 angle [105.8 (3)°], due to steric hindrance with the out-of-plane H atom in the latter case.

Complex (I) thus comprises two U atoms in completely different environments bridged by an asymmetric oxo group. The environment around U1 is comparable with that of the U<sup>III</sup> ion in the bis(tetrahydroborate) dicyclohexyl-18-crown-6 complex (Dejean *et al.*, 1987), one of the BH<sub>4</sub> groups being replaced by O7. The coordination of metal atom U2 is reminiscent of that observed in [U(BH<sub>4</sub>)<sub>4</sub>OR<sub>2</sub>] (R = methyl or ethyl; Rietz *et al.*, 1978). In these latter compounds, which are linear polymers, the three terminal BH<sub>4</sub> groups are tridentate, one of them being *trans* with respect to the ether O atom, while the two bridging BH<sub>4</sub> groups, *trans* with respect to one another, are bidentate. The first coordination sphere of the U atom is thus close to that of U2 in (I), with the same total coordination number of 14, but the ether is replaced by an oxo group in (I), which is further a molecular discrete species. No significant hydrogen-bonding interaction is present in the packing of (I), which is rather loose (66.3% filled space).

## Experimental

An NMR tube was charged with U(BH<sub>4</sub>)<sub>4</sub> (9.0 mg, 30 μmol), 18-crown-6 (7.9 mg, 30 μmol) and THF-*d*<sub>8</sub> (0.4 ml) under argon gas. After dissolution of the products, pentane was added and green crystals of (I) were formed after 4 d (4.5 mg, 35% yield).

### Crystal data

[U<sub>2</sub>(BH<sub>4</sub>)<sub>6</sub>O(C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>)]

*M<sub>r</sub>* = 845.42

Orthorhombic, *Pca*2<sub>1</sub>

*a* = 16.4251 (7) Å

*b* = 10.2676 (5) Å

*c* = 16.3550 (7) Å

*V* = 2758.2 (2) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 2.036 Mg m<sup>-3</sup>

Mo *K*α radiation

*μ* = 11.75 mm<sup>-1</sup>

*T* = 100 (2) K

Irregular, translucent light green  
0.15 × 0.12 × 0.10 mm

### Data collection

Nonius KappaCCD area-detector  
diffractometer

*φ* scans

Absorption correction: part of the

refinement model (*ΔF*)

(*DELABS* in *PLATON*; Spek,  
2003)

*T<sub>min</sub>* = 0.287, *T<sub>max</sub>* = 0.309

17685 measured reflections

5193 independent reflections

4656 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.062

*θ<sub>max</sub>* = 25.7°

### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.029

*wR*(*F*<sup>2</sup>) = 0.059

*S* = 1.03

5193 reflections

245 parameters

H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0073*P*)<sup>2</sup>  
+ 3.4303*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(*Δ*/σ)<sub>max</sub> = 0.002

*Δρ*<sub>max</sub> = 0.74 e Å<sup>-3</sup>

*Δρ*<sub>min</sub> = -0.96 e Å<sup>-3</sup>

Absolute structure: Flack (1983),

with 2489 Friedel pairs

Flack parameter: 0.006 (12)

The H atoms bound to B atoms were found in difference Fourier maps and treated as riding atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{B})$ . All other H atoms were introduced in calculated positions as riding atoms, with  $\text{C-H} = 0.97 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL2000* (Otwinowski & Minor, 1997); data reduction: *HKL2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3015). Services for accessing these data are described at the back of the journal.

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