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Structure of the Second Crystalline Form of Uranium(IV) Tetrahydroborate

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Abstract. $[U(BH_4)_4]$, $M_r = 297{\cdot}4$, orthorhombic, *Cmcm*, $a = 8{\cdot}014\,(2)$, $b = 7{\cdot}940\,(3)$, $c = 11{\cdot}673\,(3)$ Å, $V = 742{\cdot}7\,(7)$ Å^3, $Z = 4$, $D_x = 2{\cdot}66$ Mg m^{-3}, $\lambda(\text{Mo }K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 20{\cdot}60$ mm^{-1}, $F(000) = 512$, room temperature, $R = 0{\cdot}023$ for 342 observed reflections. The structure is of two-dimensional polymeric type. Each U atom is coordinated to four coplanar bridging bidentate [U—B(1) 2·84 (1) Å] and two terminal tridentate BH_4 ligands [U—B(2) 2·51 (1) Å] in *trans* position. H atoms are observed in a residual Fourier map: the most striking feature is the bending of the $U—B—H_{\text{terminal}}$ line in tridentate BH_4 [162 (6)°] which renders the three bonding H atoms inequivalent.

Introduction. The structure of $U(BH_4)_4$ was established in 1972 from both X-ray (Bernstein, Keiderling, Lippard & Mayerle, 1972) and neutron (Bernstein, Hamilton, Keiderling, La Placa, Lippard & Mayerle, 1972) single-crystal diffraction data. The surprising feature of the $U(BH_4)_4$ structure consisted in its polymeric nature in the solid state. Four of the six BH_4^- ions surrounding each U atom are attached to it by two H atoms, the two other H atoms bridging to neighboring U atoms in a polymeric structure. The two terminal tridentate BH_4 ligands in *cis* configuration complete the coordination sphere of each U atom.

We have reported (Charpin, Marquet-Ellis & Folcher, 1978) the evidence for a second crystalline form of $U(BH_4)_4$ (form II) differing by higher volatility and solubility in benzene and by its color (form I: yellow green; form II: emerald green). Though no good-quality single crystals could be obtained, we have suggested a possible two-dimensional polymerization involving terminal tridentate BH_4^- in *trans* position. Recently, we have been able to obtain in a sublimation process a mixture of both forms as single crystals suitable for an X-ray analysis and we now report the structure of $U(BH_4)_4$ form II.

Experimental. Freshly sublimated $U(BH_4)_4$ is added under Ar atmosphere to molten diphenylacetylene: a brownish color is observed, part of the borohydride is then vaporized and deposited as yellow-green $[U(BH_4)_4$ I] and emerald-green $[U(BH_4)_4$ II] crystals on the top of the tube; crystal 0·25 × 0·20 × 0·12 mm; Enraf–Nonius CAD-4 diffractometer; unit-cell parameters refined from 25 reflections in range $16 < 2\theta < 24°$; three standard reflections monitored at 100-reflection intervals, loss of 0·2% in 8 h, linearly corrected; scans by ω–2θ method; Lorentz and polarization corrections; empirical absorption correction using the program *DIFABS* (Walker & Stuart, 1983), transmission coefficients min. 0·78 and max. 1·56; 799 reflections collected, 371 unique, 342 with $I > 3\sigma(I)$; $2 < 2\theta < 40°$; $-9 \leq h \leq 0$, $-9 \leq k \leq 0$, $0 \leq l \leq 13$; structure solved by Patterson method for U, remaining atoms

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Table 1. *Positional parameters, isotropic thermal parameters and their e.s.d.'s*

	x	y	z	B_{eq}/B_{iso}(Å^2)*
U	0·000	0·28158 (8)	0·250	0·943 (8)
B(1)	−0·278 (2)	0·062 (2)	0·250	2·1 (3)
B(2)	0·000	0·234 (2)	0·463 (1)	2·7 (3)
H(11)	−0·322	0·201	0·250	2·1
H(12)	−0·122	0·042	0·250	2·1
H(13)	0·167	0·479	0·163	2·1
H(21)	0·000	0·081	0·446	2·7
H(22)	−0·125	0·297	0·420	2·7
H(23)	−0·500	0·239	0·433	2·7

* $B_{eq} = \frac{4}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23})$.

Table 2. *Bond distances* (Å) *and angles* (°)

U—B(1)	2·83 (1)	U—B(2)	2·51 (1)
U′—B(1)	2·85 (1)		
U—H(11″)	2·7 (1)	U—H(21)	2·8 (1)
U—H(12″)	2·1 (1)	U—H(22)	2·2 (1)
U—H(13)	2·3 (1)		
B(1)—H(11)	1·2 (1)	B(2)—H(21)	1·2 (1)
B(1)—H(12)	1·3 (1)	B(2)—H(22)	1·2 (1)
B(1)—H(13)	1·3 (1)	B(2)—H(23)	1·2 (1)

B(2)—U—B(2)	162·9 (5)		
H(11)—B(1)—H(12)	115 (8)	H(21)—B(2)—H(22)	109 (5)
H(11)—B(1)—H(13)	112 (5)	H(21)—B(2)—H(23)	109 (8)
H(12)—B(1)—H(13)	106 (5)	H(22)—B(2)—H(23)	110 (5)

located by difference Fourier technique; full-matrix least-squares refinement on F; scattering factors including anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). A difference Fourier map following a structure-factor calculation with $(\sin\theta)/\lambda \leq 0{\cdot}4$ Å^{-1} showed positive electron density with peak heights about 1 e Å^{-3}. Six of these peaks correspond to reasonable H-atom positions with B—H distances in the range 1·16 to 1·29 Å and H—B—H angles 106 to 115°. H atoms were not refined but only introduced in the structure-factor calculation with isotropic thermal parameters equal to those of their B atom. $R = 0{\cdot}023$, $wR = 0{\cdot}027$ ($w = 1$), $(\Delta/\sigma)_{max} = 0{\cdot}02$, $S = 3{\cdot}65$. In final difference Fourier synthesis, no peaks greater than 0·9 e Å^{-3} with the highest peaks located near the U atom; no correction for extinction; computations on a PDP 11/23 Plus with programs from Enraf–Nonius *SDP* (Frenz, 1983).

Discussion. Positional and thermal parameters are given in Table 1 and important bond distances and angles are listed in Table 2.*

The structure of $U(BH_4)_4$ II, like that of $U(BH_4)_4$ I, is of polymeric type. In uranium borohydride complexes, the B atoms are connected to the U atom by either triple or double hydrogen-bridge bonds, identified in the absence of neutron diffraction data by the observed U—B distance, 2·5 or 2·9 Å, respectively (Edelstein, 1981). In the present compound, four double hydrogen bridges link pairs of U atoms [two U—B(1) 2·83 (1) Å and two U′—B(1) 2·85 (1) Å] and lead to a two-dimensional molecular network, as shown in Fig. 1. Two additional tetraborohydrides in *trans* position are bonded to the U atom by three H atoms [U—B(2) 2·52 (1) Å] completing the coordination sphere of the U atom to 14 H atoms (Fig. 2). This kind of

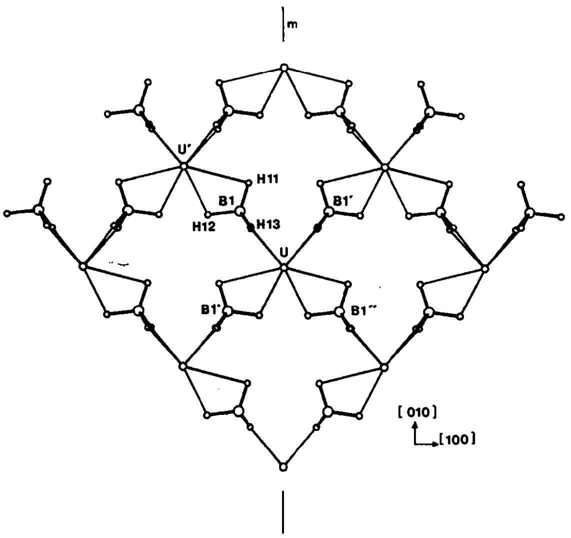

Fig. 1. An *ORTEP* view (Johnson, 1976) of the polymeric plane showing the atomic numbering scheme. [U x,y,z and U′ $\frac{1}{2}+x$, $\frac{1}{2}+y$, z; B(1) x, y, z, B(1′) $\bar{x}$, y, z, B(1″) $\frac{1}{2}+x$, $\frac{1}{2}+y$, z and B(1*) $\frac{1}{2}-x$, $\frac{1}{2}+y$, z.]

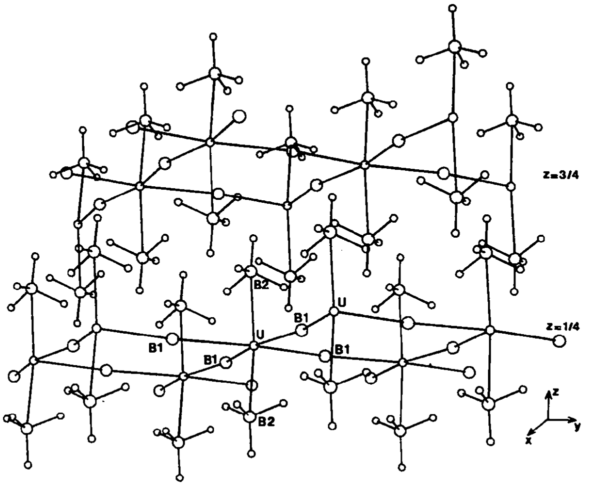

Fig. 2. Packing of $U(BH_4)_4$ II. H atoms are omitted for clarity.

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* Lists of structure factors, anisotropic thermal parameters and a full list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43893 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

two-dimensional polymerization, due to the *trans* position of the two tridentate borohydrates, confirms the structure suggested by Charpin *et al.* (1978) from an X-ray powder pattern of $U(BH_4)_4$ II.

The six B atoms form a distorted octahedron of *mm* symmetry around the U atom. The four B atoms of the bidentate borohydrides [B(1)] are coplanar and lie in the symmetry plane (001) (at $z = \frac{1}{4}$ and $\frac{3}{4}$), as do two of their H atoms, H(11) and H(12), and the U atom; the two B atoms of the tridentate borohydrides [B(2)] are located in the perpendicular symmetry plane (100). The B(2)—U—B(2) axis deviates considerably from linearity [162·9 (5)°]: this distortion may result from the packing requirement for H atoms around the U atom, as has been pointed out by Bernstein, Keiderling, Lippard & Mayerle (1972).

The U—H distances of the bidentate BH_4^- vary from 2·1 (1) to 2·7 (1) Å. The terminal H(23) atom of the tridentate ligand is oriented away from the U atom with a U—B—H(23) angle of 162 (6)°. Although the H-atom positions were not refined, the deviation by 18° from linearity seems significant: this bending renders inequivalent the three bridging H atoms and brings two of them closer to the U atom [U—H(22) 2·23 (8) Å], the third H(21) being rejected at 2·8 (1) Å. Such a geometry for the BH_4 bonding may be considered as an intermediate solution between bi- and tridentate bonding. An idealized geometry for the tridentate bonding would require the three U—H distances to be 2·34 Å [$U(BH_4)_4$ form I (Bernstein, Hamilton, Keiderling, La Placa, Lippard & Mayerle, 1972)], the terminal U—B—H being 180°, whereas in bidentate bonding the two H atoms would be at 2·45 Å from the U atom. This particular positioning of the tridentate BH_4 ligand has not so far been found in other uranium borohydrides, except in $[U(BH_4)_4(OC_4H_8)_2]$ (Charpin, Nierlich, Vigner, Lance & Baudry, 1987) and $[U(BH_4)_4\{OP(C_6H_5)_3\}_2]$ (Charpin, Nierlich, Chevrier, Vigner, Lance & Baudry, 1987).

In both forms of $U(BH_4)_4$, four bidentate and two tridentate borohydrides give the same coordination number of 14 H atoms around each U atom. Both structures are of polymeric type: they only differ by the distribution of bidentate and tridentate groups leading to a three- or two-dimensional network.

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Structure of Hashemite, $Ba(Cr,S)O_4$

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Abstract. $M_r = 250·1$, orthorhombic, *Pnma*, $a = 9·113$ (2), $b = 5·536$ (1), $c = 7·340$ (2) Å, $V = 370·3$ (1) Å^3, $Z = 4$, $D_x = 4·46$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 123·09$ cm^{-1}, $F(000) = 442·02$, $T = 293$ K, $R = 0·053$ for 541 unique reflections. Hashemite is isostructural with baryte, with Cr substituting for S in the tetrahedral site. The refined site occupancy is 84% Cr and 16% S. The average *T*—O bond length is 1·657 Å and the average O—*T*—O bond angle is 109·4°. The mean Ba—O distance is 2·966 Å. Ba is twelve-coordinated. O(1) and O(2), which lie on an (010) mirror plane, have large U_{22} thermal parameters.

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