

Inverse Cycloheptatrienyl Sandwich Complexes. Crystal Structure of $[\text{U}(\text{BH}_4)_2(\text{OC}_4\text{H}_8)_5][(\text{BH}_4)_3\text{U}(\mu\text{-}\eta^7, \eta^7\text{-C}_7\text{H}_7)\text{U}(\text{BH}_4)_3]$

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The anions $[\text{X}_3\text{U}(\mu\text{-}\eta^7, \eta^7\text{-C}_7\text{H}_7)\text{UX}_3]^-$ ($\text{X} = \text{NEt}_2$ or BH_4) have been obtained by treatment of UX_4 with $\text{K}[\text{C}_7\text{H}_9]$; the cation $[\text{U}(\text{BH}_4)_2(\text{thf})_5]^+$ was formed by protonation of $[\text{U}(\text{BH}_4)_3(\text{thf})_3]$ with $[\text{NHET}_3][\text{BPh}_4]$ in tetrahydrofuran (thf).

An aromatic hydrocarbon ligand is capable of forming bonds to metals on both faces of its planar π -electron system and inverse sandwich compounds containing an $\text{M}(\mu\text{-}\eta^n, \eta^n\text{-C}_n\text{H}_n)\text{M}'$ unit are known for $n = 5, 6$ and 8 .¹ Here we present the first examples of such complexes with $n = 7$: $[\text{K}(18\text{-crown-6})][(\text{NEt}_2)_3\text{U}(\mu\text{-}\eta^7, \eta^7\text{-C}_7\text{H}_7)\text{U}(\text{NEt}_2)_3]$ **1** (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) and $[\text{U}(\text{BH}_4)_2(\text{OC}_4\text{H}_8)_5][(\text{BH}_4)_3\text{U}(\mu\text{-}\eta^7, \eta^7\text{-C}_7\text{H}_7)\text{U}(\text{BH}_4)_3]$ **3**. While the chemistry of the $\eta\text{-C}_7\text{H}_7$ compounds of the early transition metals has been considerably developed during the last ten years,² no cycloheptatrienyl complex of an f-element has been so far characterized.³

The $[(\text{NEt}_2)_3\text{U}(\mu\text{-}\eta^7, \eta^7\text{-C}_7\text{H}_7)\text{U}(\text{NEt}_2)_3]^-$ anion was formed in toluene (25 cm³) by treatment of the amide complex $[\text{U}(\text{NEt}_2)_4]$ (453 mg) with 1 equiv. of the potassium salt of the cycloheptadienyl anion; after stirring for 5 d at 65 °C, the precipitate was filtered off, extracted in thf and the brown powder of $\text{K}[(\text{NEt}_2)_3\text{U}(\mu\text{-}\eta^7, \eta^7\text{-C}_7\text{H}_7)\text{U}(\text{NEt}_2)_3]$ (193 mg, 43%) was obtained after evaporation of the solvent. In the presence of 18-crown-6 (49 mg), brown crystals of **1** were isolated from thf-pentane (183 mg, 32% from $[\text{U}(\text{NEt}_2)_4]$). The product was characterized by its elemental analyses (C, H, N, K) and ¹H NMR spectrum;† the narrow and well resolved resonances were characteristic of an uranium(IV) derivative, thus confirming that the formal charge of the C_7H_7 ligand is -3 .⁴

Synthesis of $\text{K}[(\text{BH}_4)_3\text{U}(\mu\text{-}\eta^7, \eta^7\text{-C}_7\text{H}_7)\text{U}(\text{BH}_4)_3]$ **2** from $[\text{U}(\text{BH}_4)_4]$ and $\text{K}[\text{C}_7\text{H}_9]$ was impeded by the concomitant formation of $[\text{U}(\text{BH}_4)_3]$, resulting from the reduction of the uranium tetraborohydride by the potassium reagent; this obstacle was also encountered during the preparation of the $[\text{U}(\eta\text{-dienyl})(\text{BH}_4)_3]$ complexes.⁵ The two products **2** and $[\text{U}(\text{BH}_4)_3(\text{thf})_3]$, obtained in the ratio 40:60, presented similar solubilities and could not be separated; they were characterized only by their ¹H NMR spectra.† As we thought that the phosphine adduct $[\text{U}(\text{BH}_4)_3(\text{dmpe})_2]$ ⁶ ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) would be more soluble than $[\text{U}(\text{BH}_4)_3(\text{thf})_3]$, we treated $[\text{U}(\text{BH}_4)_4]$ (157 mg) in diethyl ether (25 cm³) with $\text{K}[\text{C}_7\text{H}_9]$ (77 mg) in the presence of dmpe (176 μl). The reaction mixture was stirred for 2 h at 20 °C, and after evaporation, the residue was extracted in thf; the solution was filtered and evaporated, leaving a brown powder (189 mg) containing the uranium trisborohydride (60%) and the desired product **2** (40%). This experiment was repeated about ten times and the proportion of **2** obtained varied from 25 to 40% (by NMR spectroscopy). During the attempted purification of **2**, red crystals along with a beige powder were deposited from thf-pentane; X-ray crystal structure analysis revealed that these were in fact $[\text{U}(\text{BH}_4)_2(\text{thf})_5][(\text{BH}_4)_3\text{U}(\mu\text{-}\eta^7, \eta^7\text{-C}_7\text{H}_7)\text{U}(\text{BH}_4)_3]$ **3**.‡

The crystals of **3** are composed of discrete cation-anion pairs. The inverse sandwich structure of the anion is shown in Fig. 1. The bridging C_7H_7 ligand and three BH_4 groups form a distorted tetrahedron around each uranium atom; the short U-B distances are characteristic of tridentate borohydride ligands.⁷ The average U-C bond distance is 2.69(2) Å and may be compared with those determined in $[\text{U}(\eta\text{-C}_5\text{H}_5)(\text{BH}_4)_3]$ ⁵ [2.66(6) Å] and $[\text{U}(\eta\text{-C}_8\text{H}_8)(\text{BH}_4)_2(\text{OPPh}_3)]$ ⁸ [2.68(2) Å]. The seven-membered ring is planar within $\pm 0.02(3)$ Å and is parallel to the planes defined by the three boron atoms of each

$\text{U}(\text{BH}_4)_3$ unit. The two uranium atoms are separated by 4.263(8) Å and the U(1)-ring centroid-U(2) axis is perpendicular to the cycloheptatrienyl plane. The ORTEP drawing of the cation is shown in Fig. 2. The uranium atom is in a quite perfect pentagonal-bipyramidal arrangement with the tridentate borohydride ligands in apical positions.

The cationic $\text{U}(\text{BH}_4)_2^+$ fragment was previously found inserted into the dicyclohexyl-(18-crown-6) ether (dcc), in the complex $[\text{U}(\text{BH}_4)_2(\text{dcc})][\text{UCl}_5(\text{BH}_4)]$ which was obtained accidentally after partial oxidation of $[\text{U}_3(\text{BH}_4)_9(\text{dcc})_2]$ in

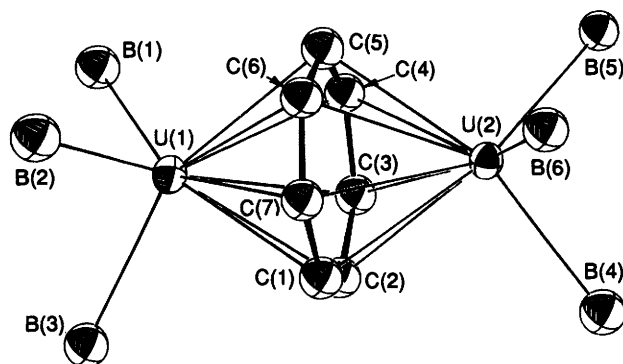


Fig. 1 The X-ray crystal structure of the anion in **3**. Only the important interatomic distances (Å) and angles (°) for one of the two independent anions in the asymmetric unit are given: $\langle \text{U}(1)\text{-B} \rangle$ 2.58(2), $\langle \text{U}(1)\text{-C} \rangle$ 2.69(2), U(1)-Cen 2.14(3), $\langle \text{U}(2)\text{-B} \rangle$ 2.59(4), $\langle \text{U}(2)\text{-C} \rangle$ 2.67(2), U(2)-Cen 2.11(3), B(1)-U(1)-B(2) 96(1), B(1)-U(1)-B(3) 99(1), B(2)-U(1)-B(3) 97(1), B(1)-U(1)-Cen 119(1), B(2)-U(1)-Cen 121(1), B(3)-U(1)-Cen 120(1), B(4)-U(2)-B(5) 99(1), B(4)-U(2)-B(6) 95(1), B(5)-U(2)-B(6) 97(1), B(4)-U(2)-Cen 121(1), B(5)-U(2)-Cen 120(1), B(6)-U(2)-Cen 120(1), U(1)-Cen-U(2) 179(2); Cen is the centroid of the cycloheptatrienyl ring.

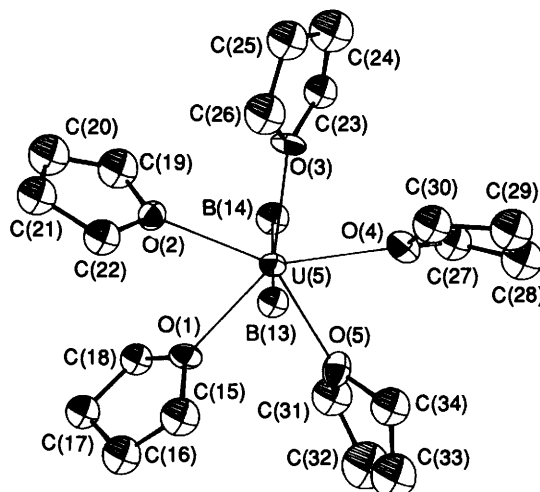


Fig. 2 The X-ray crystal structure of the cation in **3**. Only the important interatomic distances (Å) and angles (°) for one of the two independent cations in the asymmetric unit are given: U(5)-B(13) 2.72(4), U(5)-B(14) 2.71(4), $\langle \text{U}(5)\text{-O} \rangle$ 2.56(1), B(13)-U(5)-B(14) 176(1), $\langle \text{B}(13)\text{-U}(5)\text{-O} \rangle$ 90(4), $\langle \text{B}(14)\text{-U}(5)\text{-O} \rangle$ 90(4), $\langle \text{O}(n)\text{-U}(5)\text{-O}(n+1) \rangle$ 72(2).

dichloromethane.⁹ We found that the cation $[\text{U}(\text{BH}_4)_2(\text{thf})_5]^+$ could be directly and easily synthesized in almost quantitative yield by protonation of $[\text{U}(\text{BH}_4)_3(\text{thf})_3]$ (405 mg) with $[\text{NHEt}_3][\text{BPh}_4]$ (342 mg) in thf (25 cm³); after 1 h at 20 °C, the solution was evaporated, leaving brown microcrystals of $[\text{U}(\text{BH}_4)_2(\text{thf})_5][\text{BPh}_4]$ **4**. This complex was characterized by its elemental analyses (C, H, B) and ¹H NMR spectrum and its crystal structure¹⁰ showed that the geometrical parameters of the cation $[\text{U}(\text{BH}_4)_2(\text{thf})_5]^+$ were identical in both compounds **3** and **4**. Reaction of **4** with $\text{K}[\text{C}_5\text{R}_5]$ (R = H, Me) gave successively the neutral compounds $[\text{U}(\text{C}_5\text{R}_5)(\text{BH}_4)_2]$ and the anions $[\text{U}(\text{C}_5\text{R}_5)_2(\text{BH}_4)_2]^-$ (NMR experiments).^{5,11}

In conclusion, we have prepared the first inverse sandwich complexes with the C₇H₇ ligand and found an entry into the chemistry of the cycloheptatrienyl compounds of uranium. We have also described the synthesis of $[\text{U}(\text{BH}_4)_2(\text{thf})_5]^+$, a very rare example of a uranium(III) cation.¹²

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Footnotes

† ¹H NMR spectroscopic data (60 MHz, 30 °C, [²H₈]thf, J in Hz: **1**, δ 6.12 (24 H, q, J 6, CH₂), 3.23 (24 H, s, 18-crown-6), 1.49 (36 H, t, J 6, Me), -50.70 (7 H, s, C₇H₇); **2**, δ 63.43 (24 H, q, J 85 Hz, BH₄), -47.57 (7 H, s, C₇H₇); **4**, δ 13.9 (8 H, w_{1/2} 450 Hz, BH₄), 7.72, 6.91 (20 H, m, Ph).

‡ Crystal data for **3**: C₂₇H₇₉B₈O₅U₃, triclinic, space group $P\bar{1}$, $a = 12.754(8)$, $b = 15.471(9)$, $c = 24.136(8)$ Å, $\alpha = 98.99(8)$, $\beta = 96.35(8)$, $\gamma = 90.60(9)^\circ$, $U = 4673(5)$ Å³, $Z = 4$, $D_c = 1.82$ g cm⁻³, $\mu = 98.62$ cm⁻¹, 2θ max = 40°. Diffraction data were recorded on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å). 4216 reflections with $I > 3\sigma(I)$ were considered observed out of 8700 unique data collected. The structure was solved by the heavy-atom method and refined by full-matrix least squares (F) with anisotropic thermal parameters for U and O atoms; H atoms were not introduced. The final residuals were $R = 0.037$, $R_w = 0.042$ ($w = 1$). Atomic coordinates, bond lengths and angles and

thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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