Synthesis and Crystal Structure of [K($C_{12}H_{24}O_6$)][U(η-C_7H_7)$_2$], The First Cycloheptatrienyl Sandwich Compound

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The title compound was prepared by treating a mixture of UCl_4 and K with C_7H_8 or by reacting UCl_4 with KC_7H_9; the crystal structure shows that the two C_7H_7 ligands are planar, parallel and perpendicular to the linear axis defined by the uranium atom and the ring centroids.

Sandwich complexes have attracted a sustained attention since the birth of modern organometallic chemistry, marked with the discovery of ferrocene.[1] These compounds, in which a metal atom or ion is centrally located between two aromatic hydrocarbon ligands C_nH_n, are well known for n = 5, 6 and 8 but for n = 7, none has been authenticated so far. Here we present the synthesis and crystal structure of such a complex, [K(18-crown-6)] [U(η-C_7H_7)$_2$] **1**. After the inverse-sandwich compounds K[X_3U(μ-η^7,η^7-C_7H_7)UX_3] (X = NEt_2, BH_4), **1** is a new example of a cycloheptatrienyl complex of an f-element.[2]

The bis(cycloheptatrienyl)uranium anion [U(η-C_7H_7)$_2$]$^-$ was formed in THF (50 cm^3) by treating a mixture of uranium tetrachloride (212 mg) and potassium (109 mg) with an excess of cycloheptatriene (1030 mg). After stirring for 5 h at 20 °C, the solution was filtered and evaporated to dryness, leaving a green powder of K[U(η-C_7H_7)$_2$] (200 mg, 78%). In the presence of 18-crown-6, (147 mg), dark green crystals of **1** were isolated from THF(210 mg, 52%). This reaction of UCl_4 contrasts with those of the early transition metal chlorides which, under similar conditions, gave the complexes [M(η^6-C_7H_8)$_2$] and/or [M(η^7-C_7H_7)(η^5-C_7H_9)].[3,4] The vanadium derivative [V(C_7H_7)$_2$][BF_4]$_2$ was prepared by hydride abstraction from [V(C_7H_8)$_2$], but it is unclear whether this compound adopts a sandwich structure.[4] Complex **1** was alternatively prepared in 40% yield from a mixture of UCl_4 or U(BH_4)$_4$ and 4 equiv. of KC_7H_9 in THF; the reaction was immediate and by addition of 18-crown-6 to the filtered solution, thin needles of the product were crystallized. It had been previously found that the cycloheptadienyl anion $C_7H_9^-$ could be readily converted into the cycloheptatrienyl trianion $C_7H_7^{3-}$ in the presence of lanthanide or actinide chlorides.[5] Compound **1** gave satisfactory elemental analyses (C, H, K); its ^{1}H NMR spectrum (60 MHz, 30 °C, in [$^2H_8$]THF) shows a broad resonance at δ −38.7 ($w_{1/2}$ = 400 Hz), corresponding to the equivalent ring hydrogens.

The crystals of **1** are composed of discrete cation–anion pairs.† The [K(18-crown-6)]$^+$ cation displays the expected structural parameters; ORTEP drawings of the anion are shown in Fig. 1 together with selected data. The sandwich structure has C_{2h} symmetry; the mirror plane contains the U and C(4) atoms. The cycloheptatrienyl ligands are planar within ±0.02(2) Å and exhibit the regular heptagonal geometry which is almost invariably found in other η-C_7H_7 compounds, with C–C distances and C–C–C angles averaging respectively 1.37(7) Å and 129(3)°. The two rings are parallel in a staggered conformation and are perpendicular to the linear axis defined by the ring centroids and the metal atom. The uranium–carbon bond distances, which are equal within experimental error and average 2.53(2) Å, are shorter than those found in the η-C_7H_7 bridged anion [(BH_4)$_3$U(μ-η^7,η^7-C_7H_7)U(BH_4)$_3$]$^-$ [2.69(2) Å]; they are also significantly shorter than the U–C(ring) bond lengths in cyclopentadienyl and cyclooctatetraene uranium(IV) compounds, which typically range from 2.65 to 2.80 Å {2.647(4) Å in [U(η-C_8H_8)$_2$]}.[6] Similar structural features were observed in cycloheptatrienyl complexes of the early transition elements,[7] and have been explained by an electron transfer from the metal toward the ligand, corresponding to an increase of the metal valency.[8,9]

The question of the metal oxidation state in cycloheptatrienyl compounds is much debated.[9,10] The C_7H_7 ligand has been classified as uninegative,[8,11] while both a +1 and a −3 formal charge satisfy the Hückel $4n + 2$ rule for aromaticity. If the cycloheptatrienyl ligand is regarded as $C_7H_7^+$ or $C_7H_7^-$, the formal oxidation state of uranium in the anion [U(η-C_7H_7)$_2$]$^-$

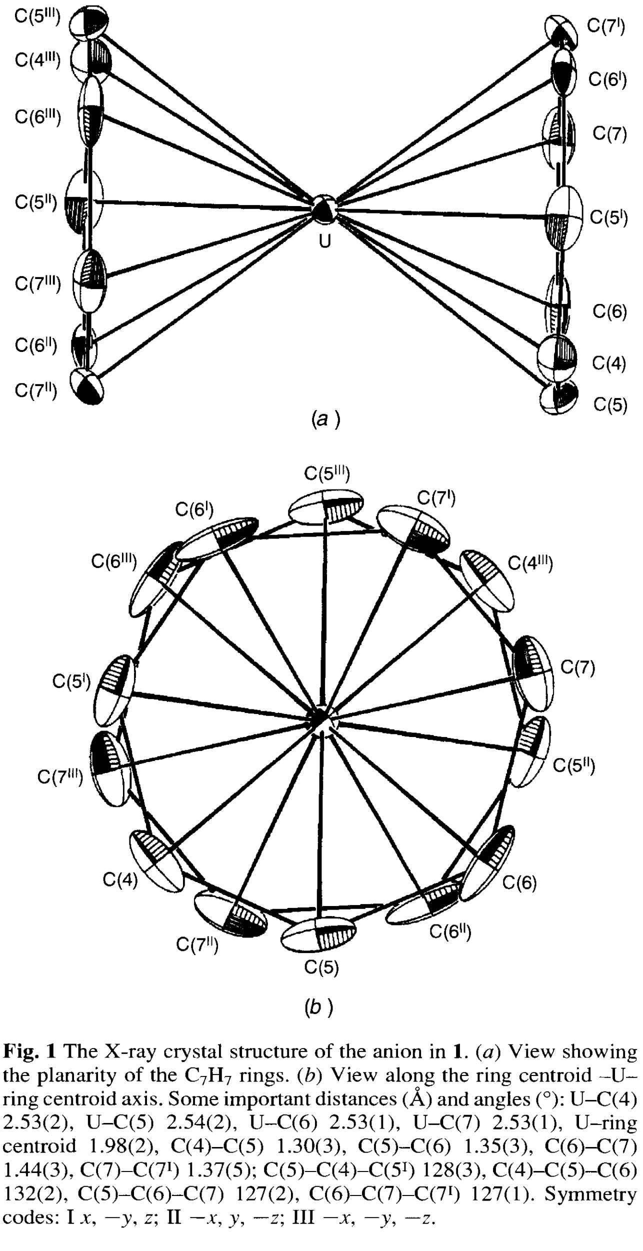

Fig. 1 The X-ray crystal structure of the anion in **1**. (*a*) View showing the planarity of the C_7H_7 rings. (*b*) View along the ring centroid–U–ring centroid axis. Some important distances (Å) and angles (°): U–C(4) 2.53(2), U–C(5) 2.54(2), U–C(6) 2.53(1), U–C(7) 2.53(1), U-ring centroid 1.98(2), C(4)–C(5) 1.30(3), C(5)–C(6) 1.35(3), C(6)–C(7) 1.44(3), C(7)–C(7^I) 1.37(5); C(5)–C(4)–C(5^I) 128(3), C(4)–C(5)–C(6) 132(2), C(5)–C(6)–C(7) 127(2), C(6)–C(7)–C(7^I) 127(1). Symmetry codes: I x, $-y$, z; II $-x$, y, $-z$; III $-x$, $-y$, $-z$.

would be −III or +I respectively, which is very unlikely. In terms of a formalism, the best description of the cycloheptatrienyl ligand is as $C_7H_7^{3-}$, the uranium being in the +V oxidation state.[10] Further physical and chemical studies will give a better insight into the U–η-C_7H_7 bonding.

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Footnote

† *Crystal data for* **1**: $C_{26}H_{38}KO_6U$, monoclinic, space group $C2/m$, a = 12.029(4), b = 13.683(3), c = 9.690(4) Å, β = 119.70(3)°, V = 1385.3(9) Å^3, Z = 2, D_c = 1.735 g cm^{-3}, μ = 57.39 cm^{-1}, $F(000)$ = 706. A single crystal of approximate dimensions 0.400 × 0.200 × 0.100 mm was introduced into a thin-walled Lindeman glass tube in an inert atmosphere dry-box. Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) with ω–2θ scans. Three standard reflections were measured after each hour, a decay was observed (12% in 13 h) and was linearly corrected. An empirical absorption correction was applied (transmission min., 1.042; max., 1.566).[12] The structure was solved from Patterson and Fourier syntheses and refined by full-matrix least squares (F) with anisotropic thermal parameters; H-atoms were not introduced. Minimized function: $\Sigma w(\Delta F)^2$, with w = 1; final R values: R = 0.034, R_w = 0.044 for 673 observed reflections with $I > 3\sigma(I)$, S = 1.21, $(\Delta/\sigma)_{max}$ = 0.05, highest peak in the final difference Fourier map = 0.86 e Å^{-3}. Crystallographic calculations were carried out using the MolEN package on a VAX 4200 computer.[13] 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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