Letter

Uranium complexes with dianionic *O*-methylated calix[4]arene ligands

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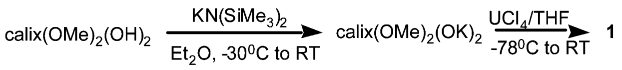
Introduction of the dianionic 25,27-*O*-dimethylated 5,11,17,23-tetra-*tert*-butylcalix[4]arene spectator, L^{2-}, to a uranium (IV) centre gave the cyclic trimeric complex 1, which was structurally characterised; complex 1 serves as a useful starting material for further derivatisation.

Calixarenes constitute a class of preorganised molecules[1] that are now regularly employed as anionic ancillary ligands in transition metal organometallic chemistry. Attractive features of these ligands include the wide scope for steric and electronic tuning attainable by substitution or functionalisation of the upper and lower rims and the possibility of frontier metal orbital manipulation by choice of the calixarene symmetry.[2] For example, the frequently used and commercially available 5,11,17,23-tetra-*tert*-butylcalix[4]arene backbone can act as a tetraanionic, aryloxide type ligand or be partially *O*-alkylated or -silylated, giving rise to mixed donor tri-, bis- and mono-aryloxide ether ligands. The transition metal organometallic chemistry of anionic calixarenes is now well advanced mainly due to the pioneering work of Floriani and his coworkers,[3] who have shown that various organometallic functional groups such as alkenes, alkynes, dienes, alkylidenes and alkylidynes can be successfully stabilised, giving rise to catalytically active complexes. The latter have been considered as models of metal oxide surfaces.

In contrast, organometallic complexes of anionic calixarenes with actinides are unknown. This is in part due to the scarcity of suitable actinide complexes[4] in which the anionic calixarene acts as an ancillary ligand. To the best of our knowledge there are only four non uranyl anionic calixarene complexes: the μ^3-oxo-bridged triangular mixed valence U(VI)–U(VI)–U(V) compound [{UCl(*p*-*tert*-butylcalix[4]arene-4H)}$_3$O], the μ^2-oxo-bridged dinuclear U(V) species [pyH]$_2$[{U(*p*-*tert*-butylcalix[5]arene-5H)}$_2$O], the U(VI) species [U(*p*-*tert*-butylcalix[6]arene-3H)$_2$], which features a homoleptic phenoxide uranium (VI) centre,[5a] and a mixed uranium (VI) lanthanum complex.[5b] U(IV) complexes are still unknown. In this letter we wish to report preliminary results on the synthesis of the first uranium(IV) complex with the dianionic 25,27-*O*-dimethylated 5,11,17,23-tetra-*tert*-butylcalix[4]arene, L^{2-}, which adopts an unprecedented symmetrical structure with bridging chlorides.

Reaction of K_2L, prepared from H_2L[6] and two equivalents of $KN(SiMe_3)_2$ in ether, with UCl_4 in THF, irrespective of the reagent ratio, gave olive-green, moisture-sensitive **1** as the only identifiable and isolable product. Yields were almost quantitative as described in the experimental (Scheme 1).



$$\text{calix(OMe)}_2\text{(OH)}_2 \xrightarrow[\text{Et}_2\text{O, -30}^0\text{C to RT}]{\text{KN(SiMe}_3\text{)}_2} \text{calix(OMe)}_2\text{(OK)}_2 \xrightarrow[\text{-78}^0\text{C to RT}]{\text{UCl}_4\text{/THF}} \mathbf{1}$$

Scheme 1

The successful isolation of the compound is critically dependent on the method of introduction of the calixarene moiety and the reaction conditions. No products could be isolated when Li_2L was used or in solvents other than THF. In addition, we were unable to prepare **1** by reaction sequences involving aminolysis of $U(NEt_2)_4$ or $U[N(SiMe_3)_2]_3Cl$ and H_2L. Finally, 25,27-*O*-trimethylsilylated calix[4]arenes or their dipotassium salts gave intractable mixtures.

Compound **1** was crystallised from light petroleum. Analytical data are consistent with the presence of one calixarene ligand and one metal centre, while the isotropically shifted ^{1}H-NMR spectrum is consistent with a local C_2 symmetric solution structure.

The structure of **1** in the solid state as determined by X-ray diffraction is shown in Fig. 1; the depiction of the coordination spheres of the trimetallic core is given in Fig. 2. Selected bond lengths and angles for **1** are given in Table 1. The molecule crystallises as a cyclic trimer, with the three uranium atoms defining approximately an equilateral triangle [U(1)–U(2)–U(1_2) 59.2(4)°, U(2)–U(1)–U(1_2) 60.3(4)°]. Two chlorine atoms are bridging each edge of the triangle. The atoms U1 and U1_2 are symmetry related and U2 is unique. The coordination polyhedron around each metal can be best described as a square-face bi-capped trigonal prism, with short [2.085(5)–2.101(5) Å] uranium aryloxide and long [2.606(5)–2.635(5) Å] uranium ether bonds. The long [4.455(5)–4.507(5) Å] intermetallic distances rule out any metal-metal interaction. The calixarene backbone is in the cone conformation. The angles subtended around the aryloxide oxygen atoms are linear

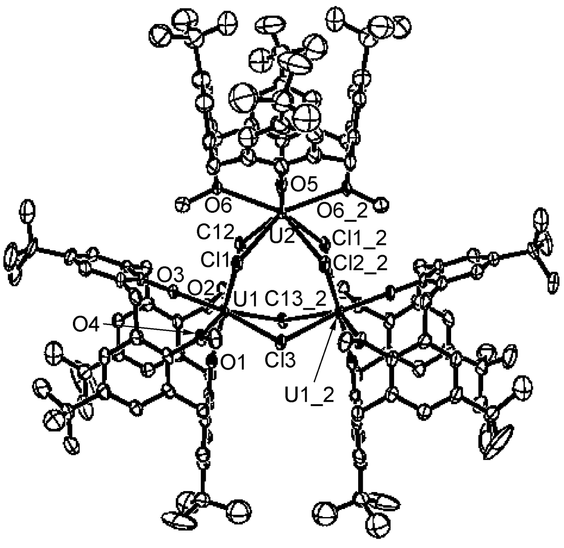


Fig. 1 ORTEP representation of the structure of **1** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

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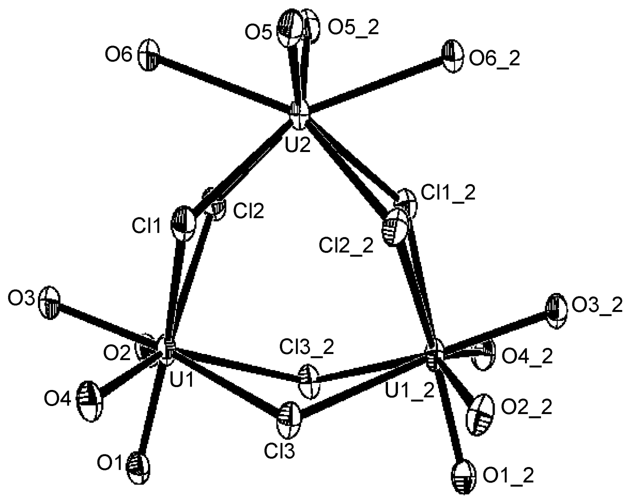

Fig. 2 Representation of the triangular metal core and the coordination spheres of the uranium atoms.

[171.8(5)–179.6(4)°], indicating substantial π-bonding with the metal. It is interesting to note that no ligation of the THF reaction solvent is observed, supporting electronic and steric saturation of the metal by the dianionic calixarene (formally an X_2L_2 8-electron donor, ignoring π-bonding). Complex **1** is a rare example of a mixed chloro aryloxide of uranium (IV).

There are only two types of triangular, chloride-bridged structural motifs in uranium chemistry. The first is found in $[Cp^*{}_2U(\mu\text{–}Cl)]_3$, a U(III) species[7] with symmetrical single chloride bridges, and the second in a $[U_3(\mu^2\text{–}Cl)_3(\mu^3\text{–}Cl)_2]$ core found in cationic complexes stabilised by $\eta^5\text{–}C_5H_5$ or $\eta^6\text{–}C_6H_6$ interactions.[8] Furthermore, the core observed in **1** has been encountered in cationic mixed-valence complexes of early transition metals (V, Zr, Nb) with capping η^6-arenes.[9,10] These were first prepared by Fischer using reductive Friedel–Crafts conditions ($AlCl_3/Al/C_6H_6$). In an analogous way UCl_4 was reduced to a 'cluster' with a $[U_3(\mu^2\text{–}Cl_3)(\mu^3\text{–}Cl_2)]$ core.[7] The factors favouring the adoption of this structure in **1** are not yet clear.

Substitution of the chlorides in **1**, especially with anionic nucleophiles like alkyls and amides, is facile. The reactions proceed smoothly in ether and the brown microcrystalline products, soluble in hydrocarbon solvents, are extremely air-sensitive. Attempts to determine their crystal structures and study their reactivity are in progress.

Experimental

Syntheses

All manipulations were carried out under inert atmosphere (N_2) by employing standard Schlenkware techniques or in a Braun Unilab glovebox. Solvents were dried and distilled just before use; the light petroleum used had a b.p. 40–60 °C. The starting materials UCl_4[11] and LH_2[6] were prepared by following published methods. All other chemicals were commercially available and were used as received.

Table 1 Selected bond lengths (Å) and angles (°) for **1**

O(1)–U(1)	2.087(12)	U(2)–Cl(1)–U(1)	104.83(7)
O(2)–U(1)	2.619(6)	U(2)–Cl(2)–U(1)	104.54(7)
O(3)–U(1)	2.101(5)	U(1)–O(1)–C(13)	171.8(5)
O(4)–U(1)	2.606(5)	U(1)–O(2)–C(28)	115.0(5)
Cl(1)–U(1)	2.862(2)	U(1)–O(3)–C(39)	179.6(4)
Cl(1)–U(2)	2.826(2)	U(1)–O(4)–C(1)	115.2(5)
Cl(2)–U(1)	2.852(2)	U(2)–O(5)–C(47)	179.5(7)
Cl(2)–U(2)	2.847(2)	U(2)–O(6)–C(58)	117.0(4)
Cl(3)–U(1)	2.849(2)		

Preparation of K_2L. To a solution of H_2L (0.68 g, 1 mmol) in ether (30 cm^3) at -50 °C was added by cannula a solution of $KN(SiMe_3)_2$(0.4 g, 2 mmol) in the same solvent (10 cm^3). After warming to room temperature and stirring for 2 h the volatiles were removed under reduced pressure, the white residue was washed twice with light petroleum and dried under vacuum. This white microcrystalline material was used further for the preparation of **1**. Yield: 0.58 g, 78%.

Preparation of 1. A solution of K_2L (0.4 g, 0.53 mmol) in THF (10 cm^3) was added by cannula to a cold (-78 °C) solution of UCl_4 (0.2 g, 0.53 mmol) in the same solvent (30 cm^3). The green reaction mixture became lighter as it warmed up and olive-green at room temperature. After stirring for 5 h the volatiles were removed under reduced pressure, the residue was extracted into light petroleum (3×30 cm^3) and filtered through Celite. Concentration of the extracts and cooling (-20 °C) gave olive-green air-sensitive crystals. Yield: 0.47 g, 92% in two crops. Anal. found: C: 55.45, H: 6.05; calcd for $(C_{46}H_{58}O_4Cl_2U)_3$: C 56.15, H, 5.94%. ^{1}H-NMR, C_6D_6: δ -45.5 (s, 6H, OMe), -16.5 (s, 2H, CH_2), -6.6 (s, 2H, CH_2), 13 (s, 2H, CH_2), 20 (s, 2H, CH_2), -11.5 and 20 (s, 4H each, aromatic), 7.5 and 9.5 (s, 18H each, *tert*-butyl).

X-Ray crystallography

The crystals of **1** were kept under nujol and mounted onto a glass fibre. Refinements and all data processing was completed using the WinGX[12] package. All hydrogens were assigned using a riding model. Unassigned density peaks are located within 0.6 Å of a uranium centre and do not represent an atom. Due to large disorder in the tertiary butyl groups attached to the phenyl rings there is a large maximum refinement shift value, which could not be reduced by increasing the number of refinements or by damping the structure; this problem is due to the poor quality of the crystals from which the data were collected.

Crystal data: for **1**: $C_{138}H_{170}Cl_6O_{12}U_3$,$M = 2947.53$ g mol^{-1}, olive-green crystal, dimensions $0.1 \times 0.08 \times 0.03$ mm^3, monoclinic $C2/C$ (no.15), $a = 20.796(4)$, $b = 36.322(7)$, $c = 23.030(5)$ Å, $\beta = 101.92(3)°$, $U = 17\,021(6)$ Å^3, $T = 150$ K, $Z = 4$, $\rho = 1.150$ mg m^{-3}, μ(Mo-Kα) $= 2.986$ mm^{-1}, $\lambda = 0.71073$ Å, 52 642 reflections measured, 19 213 unique ($R_{int} = 0.0696$), which were used in all calculations. The final $wR(F^2)$ was 0.2183 (all data) and $R = 0.0685$ [$F > 2\sigma(F)$]. CCDC reference number 192 743. See http://www.rsc.org/suppdata/nj/b2/b212092e/ for crystallographic files in CIF or other electronic format.

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