

Uranium(IV) complexes of calix[*n*]arenes (*n* = 4, 6 and 8)

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Reaction of UCl_4 with calix[*n*]arenes (*n* = 4, 6 and 8) in THF or pyridine gave the mononuclear $[\text{UCl}_2(\text{calix}[4]\text{arene} - 2\text{H})(\text{THF})_2]$, bis-binuclear $[\text{U}_2\text{Cl}_2(\text{calix}[6]\text{arene} - 6\text{H})(\text{THF})_3]_2$ and trinuclear $[\text{Hpy}]_6[\text{U}_3\text{Cl}_{11}(\text{calix}[8]\text{arene} - 7\text{H})]$ complexes, respectively, which are the first U^{IV} complexes of O-unsubstituted calixarenes.

In contrast to the versatility of calixarenes in complexes of the d-transition metals and 4f-elements,¹ the use of these macrocyclic polyphenoxide ligands in actinide chemistry has been limited principally to the synthesis of uranyl compounds² and some U^{V} and U^{VI} derivatives that resulted from the reaction of UCl_4 with *para-tert*-butylcalix[*n*]arenes (*n* = 4, 5 and 6) in the presence of adventitious traces of water or oxygen.³ The only calixarene complexes of an actinide(IV) are the tetranuclear thorium compound $[\text{Th}_4(\text{HL})(\text{H}_2\text{L})(\text{DMSO})_4(\text{OH})_3(\text{OH}_2)]$ (H_8L = *para-tert*-butylcalix[8]arene)⁴ and the recently reported uranium(IV) trimeric compound $[\text{UCl}_2\text{L}]_3$, which was prepared by treating UCl_4 with K_2L (H_2L = O-dimethylated *para-tert*-butylcalix[4]arene).⁵ It was pointed out that the successful isolation of the latter was critically dependent on the reaction conditions. In fact, uranium(IV) complexes of simple, unsubstituted calix[*n*]arenes have proved difficult to isolate and characterize, seemingly because of their extreme sensitivity to air and moisture. We found that reaction of UCl_4 with calix[*n*]arenes (*n* = 4, 6 and 8) under a rigorously inert atmosphere readily led to the formation of the mononuclear $[\text{UCl}_2(\text{calix}[4]\text{arene} - 2\text{H})(\text{THF})_2]$ (**1**), bis-binuclear $[\text{U}_2\text{Cl}_2(\text{calix}[6]\text{arene} - 6\text{H})(\text{THF})_3]_2$ (**2**) and trinuclear $[\text{Hpy}]_6[\text{U}_3\text{Cl}_{11}(\text{calix}[8]\text{arene} - 7\text{H})]$ (**3**) complexes, respectively. Here we present the synthesis and characterization of these compounds, including the X-ray crystal structures of their solvates.

Complex **1** was prepared from an equimolar mixture of calix[4]arene (100 mg) and UCl_4 (89 mg) in THF (15 mL); the solution was heated at 80 °C for 4 d and deposited green crystals of **1**·2THF (58% yield). A similar reaction of calix[6]arene (80 mg) with 2 molar equivalents of UCl_4 (95 mg) was not so straightforward and gave, after 6 d at 80 °C, a mixture containing green crystals of **2**·6THF as a major product, in *ca.* 35% yield, and a pale green powder of an unidentified compound; complex **2** could not be obtained in an analytically pure form. Because calix[8]arene is poorly soluble in THF, its reaction with 3 molar equivalents of the uranium salt was performed in pyridine; the brown solution was heated at 110 °C and green crystals of **3**·3py were collected in 34% yield after 24 h. It is noteworthy that the syntheses of the neutral compounds **1** and **2** did not require initial

deprotonation of the calixarene with a base, whereas pyridinium ions are formed in the preparation of the anionic complex **3**. These compounds were characterized by their elemental analyses (except **2**), ¹H NMR spectra,[†] and X-ray crystal structures.[‡]

A view of **1**·2THF is shown in Fig. 1 together with selected geometric data. The eight-coordinate uranium atom adopts a distorted square antiprismatic configuration, one square face being defined by the O atoms of the calixarene ligand and the other by the two Cl atoms and the O atoms of two THF molecules. The four donor atoms of the ligand are planar with a maximum deviation of 0.261(1) Å. The uranium atom is located at 1.200(1) Å from this mean plane. The macrocycle is in the distorted cone conformation, with dihedral angles between the four aromatic rings and the O₄ plane of 38.11(13), 75.92(11), 34.54(8) and 76.63(12)°. The largest angles correspond to the aromatic rings linked to the protonated O2 and O4 atoms, which are more distant than the phenoxide O1 and O3 atoms from the metal center. The U–O_{phenoxy} distances, which average 2.130(5) Å, are comparable with those in the aforementioned trimeric uranium(IV) complex of O-dimethylated *para-tert*-butylcalix[4]arene (mean value 2.09(2) Å).⁵ The angles subtended around O1 and O3 are almost linear (176.6(3) and 172.0(3)°), showing substantial π-bonding with the metal. Each of the O2H and O4H hydroxy groups is involved in a hydrogen bond with a THF molecule (O2···O7 2.670(6) and O4···O8 2.638(4) Å); the average U–O_{hydroxy} distance of 2.528(3) Å is 0.05 Å longer than that measured in $[\text{UCl}_4(\text{PrOH})_4]$.⁶ The mean values of the U–O_{THF} and U–Cl bond lengths, 2.61(3) and

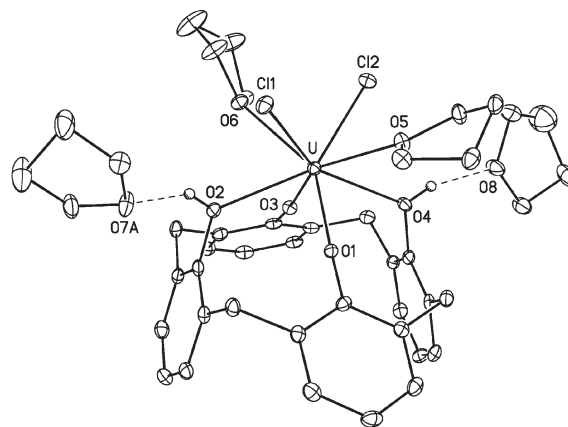


Fig. 1 View of **1**·2THF. The H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Only one position of the disordered THF molecule is represented. Selected bond lengths (Å) and angles (°): U–O1 2.135(3), U–O2 2.531(3), U–O3 2.125(3), U–O4 2.525(3), U–O5 2.579(3), U–O6 2.644(3), U–Cl1 2.7092(10) and U–Cl2 2.7297(10); U–O1–C2 176.6(3), U–O2–C9 124.3(2), U–O3–C16 172.0(3) and U–O4–C23 123.0(2).

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2.72(1) Å, respectively, are larger than the mean values of 2.49(7) and 2.64(6) Å calculated from data in the Cambridge Structural Database;⁷ these U–O and U–Cl (non-bridging) distances are however similar to those measured in [UCl₂(MeCOCHCOMe)₂(THF)₂] (U–O_{THF} 2.618(8) and U–Cl 2.684(3) Å)⁸ and [UCl₂L(py)₂] (L = hexadentate Schiff base ligand; <U–Cl> 2.73(3) Å).⁹

The centrosymmetric dimeric structure of **2**·6THF (Fig. 2) is built up from two binuclear sub-units which are linked by the O2 and O2' atoms of the calixarene ligands, in a bridging position between U1 and U1'. In the asymmetric unit, which exhibits a pseudo symmetry plane defined by the U1, U2, Cl1 and Cl2 atoms with a maximum deviation of 0.002(1) Å, U1 and U2 are attached to the macrocycle *via* three oxygen atoms each and are bridged by the two chlorine atoms; their seven-coordination environment being completed with THF molecules. The calix[6]arene ligand adopts the common 1,2,3-alternate conformation, and U1 and U2 are located at 0.404(7) and 0.718(6) Å from the O₃ plane of their phenoxide ligands; the dihedral angles between this plane and the three phenyl groups are 42.5(5), 82.6(4), 43.9(6)° and 38.2(4), 83.8(4), 36.0(6)° for the two half-molecules, respectively. The U1 atom adopts a distorted pentagonal bipyramidal configuration, with O1 and O3 in apical positions and O2, O2', O7, Cl1 and Cl2 in the basal plane with a maximum deviation of 0.245(6) Å. The coordination geometry of U2 is best described as a distorted mono-capped trigonal prism; the two triangles defined by O4, Cl1, Cl2 and O5, O6, O9 form a dihedral angle of 1.7(6)° with O8 in the capping position. With the exception of the U1–O2 and U1–O2' distances, corresponding to the bridging phenoxide groups that are expectedly longer, the average U–O_{phenoxo} distance of 2.15(4) Å is similar to that measured in the mononuclear compound **1**. The mean U–Cl bond length of 2.82(6) Å is close to those encountered in chloride-bridged uranium(IV) compounds; the average U–O_{THF} distance of 2.514(6) Å is also unexceptional.

The structure of the trinuclear anion of **3**·3py is represented in Fig. 3. The plane defined by the O2, U1, Cl1 and O6 atoms, with a

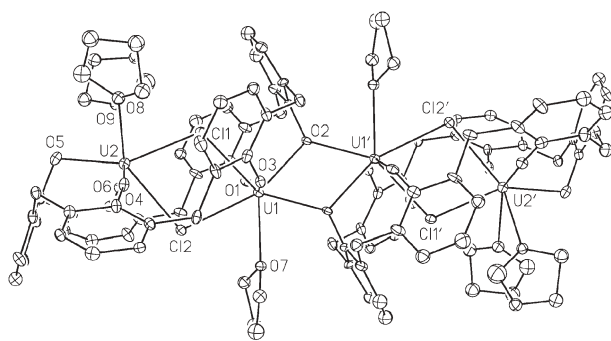


Fig. 2 View of **2**·6THF. The H atoms and solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 10% probability level. Selected bond lengths (Å) and angles (°): U1–O1 2.112(9), U1–O2 2.383(7), U1–O3 2.128(8), U1–O7 2.506(10), U1–O2' 2.372(9), U1–Cl1 2.795(4), U1–Cl2 2.865(3), U2–O4 2.142(9), U2–O5 2.227(10), U2–O6 2.123(8), U2–O8 2.518(11), U2–O9 2.518(10), U2–Cl1 2.740(4), U2–Cl2 2.888(4), U1...U2 4.5430(8) and U1...U1' 4.0726(9); U1–O1–C2 150.1(9), U1–O2–C9 111.5(7), U1–O3–C16 146.5(9), U1–O2'–C9' 130.3(7), U2–O4–C23 165.3(8), U2–O5–C30 106.6(8), U2–O6–C37 166.6(9), U1–O2–U1' 117.8(4), U1–Cl1–U2 110.31(12) and U1–Cl2–U2 104.30(11). Symmetry code: $' -x, 2 - y, -z$.

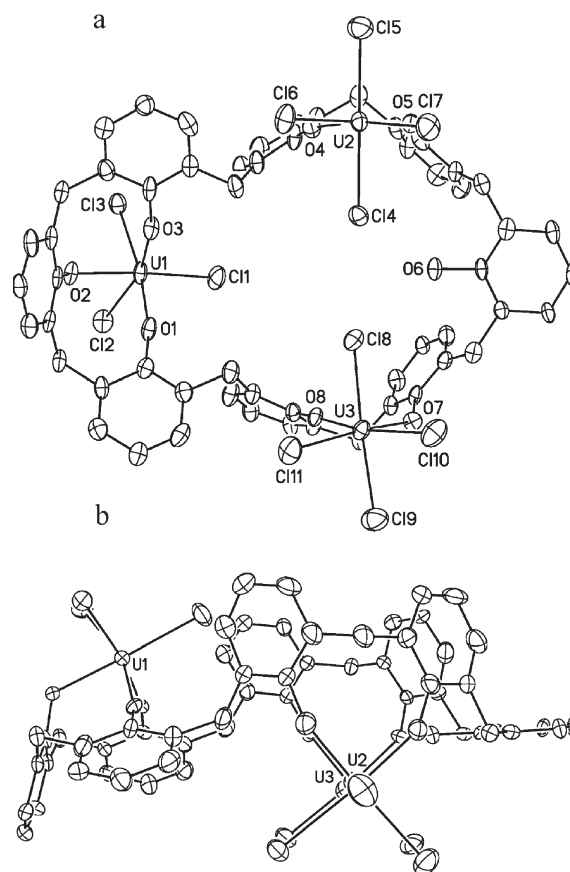


Fig. 3 Views of **3**·3py perpendicular (a) and parallel (b) to the mean O₈ plane. The H atoms and solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): U1–O1 2.127(9), U1–O2 2.244(8), U1–O3 2.120(8), U1–Cl1 2.637(4), U1–Cl2 2.704(4), U1–Cl3 2.702(4), U2–O4 2.128(9), U2–O5 2.143(8), U2–Cl4 2.693(3), U2–Cl5 2.649(4), U2–Cl6 2.663(4), U2–Cl7 2.675(4), U3–O7 2.198(7), U3–O8 2.107(8), U3–Cl8 2.653(4), U3–Cl9 2.644(5), U3–Cl10 2.684(4), U3–Cl11 2.650(4), U1...U2 8.8708(9), U1...U3 8.8110(9) and U2...U3 8.8968(11); U1–O1–C2 167.0(8), U1–O2–C9 125.5(7), U1–O3–C16 159.5(8), U2–O4–C23 161.3(8), U2–O5–C30 144.9(7), U3–O7–C44 135.0(7) and U3–O8–C51 169.8(7).

maximum deviation of 0.055(4) Å, is a pseudo mirror plane for the complex. The eight oxygen atoms of the calixarene ligand are nearly coplanar, with a maximum deviation of 0.151(6) Å. Each uranium atom is six-coordinate with a *fac*-O₃Cl₃ and *cis*-O₂Cl₄ octahedral geometry for U1 and U2 or U3, respectively; the distances of these atoms from the O₈ plane are 1.327(4), –1.586(6) and –1.641(5) Å, and they form a nearly regular equilateral triangle. The O6 atom is protonated and hydrogen bonded to Cl4 (O6...Cl4 3.124(9) Å). The macrocycle adopts an unprecedented conformation, with three adjacent phenyl groups lying to one side of the O₈ plane and five to the other, though the central phenyl of the group of five lies close to that plane, dihedral angles being 37.0(3), 83.5(3), 32.3(3), 79.3(4), 79.4(3), 10.6(3), 74.0(3) and 67.5(3)°. This geometry is quite different to those previously observed for calix[8]arene derivatives, which are generally of the 'pleated loop', 'saddle' or 'propeller' type,⁷ and in particular different to that found in [W₃Cl₁₀(*para-tert*-butylcalix[8]arene – 8H)],¹² the only other trinuclear complex of a calix[8]arene, in

which the macrocycle adopts a 'propeller', twisted conformation. The electronic charge of the anionic complex is balanced by those of six pyridinium ions, five of which are hydrogen bonded to the phenoxide oxygen atoms O2 and O7 (N1...O2 2.609(13) and N3...O7 2.697(15) Å), to the chlorine atom Cl11 (N6...Cl11 3.243(18) Å) and to two pyridine nitrogen atoms (N4...N5 2.578(15) and N7...N8 3.150(18) Å); the sixth is involved in a bifurcated hydrogen bond with O6 and Cl4 (N2...O6 2.984(16) and N2...Cl4 3.318(15) Å). Due to the hydrogen bonds, the U1–O2 and U3–O7 distances (mean value 2.22(2) Å) are larger than the other U–O_{phenoxy} bond lengths, which average 2.125(12) Å, and are similar to those in **1** and **2**. The U–Cl bond lengths vary from 2.637(4) to 2.704(4) Å, with a mean value of 2.67(2) Å.

In conclusion, calix[*n*]arenes (*n* = 4, 6 and 8) were found to give stable complexes of uranium(IV) under proper experimental conditions, in which the macrocyclic ligand encompasses one, two and three metallic fragments, respectively. The crystal structure of the trinuclear compound revealed a new conformation of the calix[8]arene ligand. The reactivity of these compounds, in particular the synthesis of derivatives by substitution of the chloride groups, is currently being studied; the magnetic properties of these polynuclear complexes are also under investigation.

Notes and references

† Characterizing data: ¹H NMR (200 MHz, 22 °C in [²H₈]THF, except **3** in [²H₅]pyridine): **1**, δ –8.87 and 0.45 (2 × 4 H, –CH₂–), 6.36 and 12.96 (2 × 2 H, aromatic-H), and 6.96 and 14.89 (2 × 4 H, aromatic-H); **2**, δ = –8.01, –7.40, –6.78, 0.74, 0.92 and 2.32 (6 × 4 H, –CH₂–), 4.22, 4.68, 4.87, 5.36, 8.55, 11.96, 13.33 and 14.09 (8 × 4 H, aromatic-H), and 4.46 and 6.38 (2 × 2 H, aromatic-H); **3**, δ –4.57 and –3.61 (2 × 2 H, –CH₂–), 0.38 and 1.91 (2 × 6 H, –CH₂–), 7.71, 12.39, 13.71, 13.79, 14.91, 15.65, 16.16 (7 × 2 H, aromatic-H), 8.24 (1 H, aromatic-H), and 9.12–9.98 (9 H, m, aromatic-H). Elemental analyses (%) (calculated values in parentheses). **1**: C, 49.6 (49.4); H, 4.6 (4.3). **3**: 43.3 (44.6); H, 3.4 (3.4).

‡ Crystal data: Compound **1**·2THF: C₄₄H₅₄Cl₂O₈U, *M* = 1019.80, monoclinic, space group *P*₂₁/*c*, *a* = 18.7160(6), *b* = 11.0604(2), *c* = 21.3661(7) Å, β = 111.321(2)°, *V* = 4120.2(2) Å³, *Z* = 4, *D*_c = 1.644 g cm^{–3}, μ = 4.122 mm^{–1}, *F*(000) = 2032, *R*₁ = 0.028, *wR*₂ = 0.065, *S* = 1.027 for 7706 independent reflections (*R*_{int} = 0.045) and 515 parameters. Compound **2**·6THF: C₁₃₂H₁₅₆Cl₄O₂₄U₄, *M* = 3220.49, triclinic, space group *P* $\bar{1}$, *a* = 13.9003(6), *b* = 15.8165(7), *c* = 16.4023(10) Å, α = 71.339(2), β = 83.412(2), γ = 64.607(4)°, *V* = 3085.4(3) Å³, *Z* = 1, *D*_c = 1.733 g cm^{–3}, μ = 5.390 mm^{–1}, *F*(000) = 1576, *R*₁ = 0.070, *wR*₂ = 0.204, *S* = 1.025 for 11476 independent reflections (*R*_{int} = 0.084) and 739 parameters. Compound **3**·3py: C₁₀₁H₉₂Cl₁₁N₉O₈U₃, *M* = 2663.88, monoclinic, space group *P*₂₁/*n*,

a = 18.7818(14), *b* = 30.660(3), *c* = 19.4331(19) Å, β = 112.569(5)°, *V* = 10333.6(17) Å³, *Z* = 4, *D*_c = 1.712 g cm^{–3}, μ = 5.033 mm^{–1}, *F*(000) = 5152, *R*₁ = 0.077, *wR*₂ = 0.209, *S* = 1.021 for 19453 independent reflections (*R*_{int} = 0.129) and 1156 parameters. Data for all compounds were collected at 100(2) K on a Nonius-Kappa CCD area detector diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) and processed with HKL2000.¹³ The structures were solved by direct methods and refined by full-matrix least-squares on *F*² with SHELXTL.¹⁴ Absorption effects were empirically corrected.¹⁵ In 1·2THF, the THF molecule containing O7 is disordered over two positions. CCDC 290602–290604. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516438a

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- This conformation can also be characterized by the eight pairs of torsion angles (φ, γ) defined by the methylene links (105.2(15), –73.6(15); 78.6(15), –113.8(13); –72.1(16), –77.4(18); –93.0(17), 77.9(16); –19.3(19), 102.9(13); –103.0(13), 7.3(18); –74.5(15), 104.4(14); 56.7(18), 77.4(15)°), which gives the symbolic representation C_s (+ –, + –, – –, – +, ~0 +, – ~0, – +, + +), evidencing the 'partial cone' arrangement of the first three phenoxide units, the reversal between the two sub-units and the peculiar position of the ring attached to O6 (ref. 11).
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