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Uranium(IV) Complexes of Calix[5]arene

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The μ-oxo uranium(V) compound $[Hpy]_2[\{U(calix[5]arene–5H)\}_2(\mu_2\text{-}O)]\cdot 4py$ (**1**·4py) was the sole product isolated from the reaction of UCl_4 and calix[5]arene unless the last traces of water were eliminated by thoroughly drying the macrocyclic molecule; under such strictly anhydrous conditions, the binuclear U^{IV} complex $[Hpy]_3[U_2(calix[5]arene–5H)Cl_6]\cdot 4py$ (**2**·4py) was obtained. Treatment of $U(OTf)_3$ or $U(OTf)_4$ (OTf = OSO_2CF_3) with calix[5]arene gave the dimeric U^{IV} complex $[U(calix[5]arene–4H)(py)]_2\cdot 4py$ (**3**·4py); compound **3** was also formed when no precautions were taken to avoid the presence of traces of water, together with compound **1**. The crystal structures of the complexes were determined.

Introduction

We have recently reported on the synthesis and X-ray crystal structures of uranium(IV) complexes with calixarene ligands resulting from reactions of UCl_4 with calix[*n*]arenes (*n* = 4, 6 and 8),[1] and of UX_4 [X = Cl, MeCOCHCOMe (acac) and OSO_2CF_3 (OTf)] or $U(OTf)_3$ with the *O*-dimethylated *p*-*tert*-butylcalix[4]arene (Me_2-*t*Bucalix[4]arene).[2] As also outlined in the case of the preparation of the chloride-bridged trimeric complex $[\{U(Me_2\text{-}t\text{Bucalix[4]arene–2H})(\mu\text{-}Cl)_2\}_3]$,[3] the successful isolation of these compounds was critically dependent on the reaction conditions; in particular, the elimination of adventitious traces of water was of major importance to avoid the oxidation of the U^{IV} ion. These difficulties explain why the first attempts to prepare uranium(IV) calixarene compounds by treatment of UCl_4 with *p*-*tert*-butylcalix[*n*]arenes (*n* = 4, 5, 6) resulted in the formation of a trinuclear, μ_3-oxo-centred $[U^{VI}_2U^V]$ complex for *n* = 4, dinuclear, μ_2-oxo-centred U^V or U^{VI} complexes for *n* = 5 and a mononuclear U^{VI} homoleptic alkoxide complex for *n* = 6.[4] We encountered the same problems when we studied the reactions of UX_4 with calix[5]arene. These reactions seemed to be of special interest to us because metal complexes of calix[5]arene derivatives are rather scarce. A search of the Cambridge Structural Database (CSD, Version 5.27)[5] indicates that only six metal complexes of simple R-calix[5]arene (R = H, *tert*-butyl) have been crystallographically characterised.[4,6–9] Concerning the 5f-element compounds, apart from the binuclear U^V and U^{VI} derivatives cited above,[4] the mononuclear uranyl complex $[HNEt_3]_2[UO_2(p\text{-}tert\text{-butylcalix[5]arene–4H})]$ has also been described.[8] Here we present the synthesis and X-ray crystal structures of the U^{IV} and U^V compounds, which were obtained from reactions of UX_4 (X = Cl, OTf) with calix[5]arene.

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Results and Discussion

Reaction of UCl_4 with 1 molar equiv. of commercial calix[5]arene in pyridine at 20 °C afforded dark orange crystals of the μ-oxo uranium(V) compound $[Hpy]_2[\{U(calix[5]arene–5H)\}_2(\mu_2\text{-}O)]\cdot 4py$ (**1**·4py) in 63% yield. The synthesis of **1** is reminiscent of that of $[Hpy]_2[\{U(p\text{-}tert\text{-butylcalix[5]arene–5H)}\}_2(\mu_2\text{-}O)]$ from UCl_4 and *p*-*tert*-butylcalix[5]arene.[4] The crystal structures of both compounds are quite similar and do not merit further discussion; a view of **1** is shown in Figure 1, and selected bond lengths and angles are listed in Table 1.

As the $U^{IV} \rightarrow U^V$ oxidation during the formation of **1** likely resulted from the presence of water in the reaction mixture, it was suspected that commercial calix[5]arene was not anhydrous, and it was heated under vacuum at 130 °C for 1 d, but this had no effect on the course of the reaction. However, the TGA-DTA analysis of this macrocycle revealed a gradual endothermic process between 120 and 210 °C, with a weight loss of 0.9%, which would correspond to the release of half an included water molecule per calix[5]arene. Final drying of the latter was achieved by leaving a pyridine solution on molecular sieves (4 Å) for 5 d; the colourless solution turned pale blue and the ^1H NMR signal of the hydroxy protons shifted from δ = 10.57 to 13.75. Addition of 2 molar equiv. of UCl_4 into the anhydrous solution of calix[5]arene gave a green solution, which slowly deposited light green crystals of the uranium(IV) compound $[Hpy]_3[U_2(calix[5]arene–5H)Cl_6]\cdot 4py$ (**2**·4py) in 24% yield.

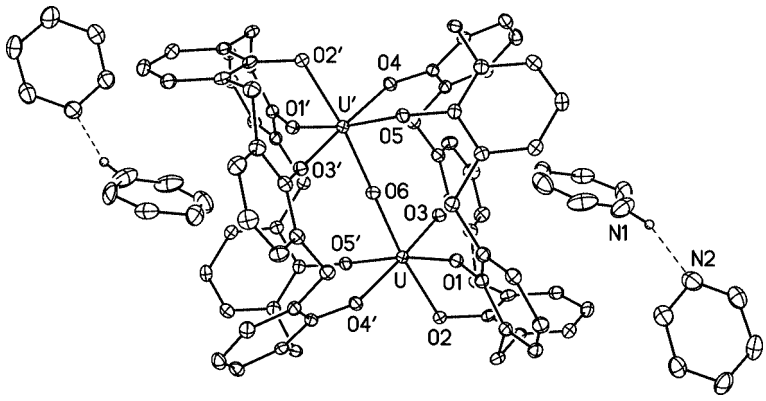

Figure 1. View of complex **1**·4py with displacement ellipsoids drawn at the 30% probability level; two solvent pyridine molecules and hydrogen atoms not involved in hydrogen bonds have been omitted; hydrogen bonds are shown as dashed lines; symmetry code: *–x*, 1 – *y*, *–z*.

Table 1. Selected bond lengths [Å] and angles [°] in compounds **1**–**3**.

1·4py	U–O1	2.157(2)	U–O1–C2	156.9(2)
	U–O2	2.171(2)	U–O2–C9	118.52(19)
	U–O3	2.149(2)	U–O3–C16	157.0(2)
	U–O4′	2.126(2)	U′–O4–C23	154.8(2)
	U–O5′	2.172(2)	U′–O5–C30	147.6(2)
	U–O6	2.08482(12)		
	symmetry code: *–x*, 1 – *y*, *–z*			
2·4py	U1–O1	2.140(7)	U1–O1–C2	158.4(7)
	U1–O2	2.144(8)	U1–O2–C9	119.3(7)
	U1–O3	2.177(7)	U1–O3–C16	155.5(7)
	U1–Cl1	2.793(3)		
	U1–Cl2	2.693(3)		
	U1–Cl3	2.693(3)		
	U2–O4	2.110(8)	U2–O4–C23	158.7(7)
	U2–O5	2.107(7)	U2–O5–C30	152.3(7)
	U2–Cl1	2.812(3)		
	U2–Cl4	2.679(3)	U1···U2	5.2862(8)
	U2–Cl5	2.650(4)		
	U2–Cl6	2.670(3)		
3·4py	U–O1	2.169(2)	U–O1–C2	177.4(2)
	U–O2	2.671(2)	U–O2–C9	97.56(19)
	U–O3	2.149(2)	U′–O2–C9	156.8(2)
	U–O4	2.239(2)	U–O3–C16	172.5(2)
	U–O5	2.674(2)	U–O4–C23	132.9(2)
	U–O2′	2.222(2)	U–O5–C30	107.63(19)
	U–N1	2.573(3)	U–O2–U′	105.46(8)
	symmetry code: 2 – *x*, 1 – *y*, 2 – *z*			

The trianionic complex, shown in Figure 2, represents a unique example of two metal atoms bound to a single calix[5]arene ligand. The structure shows a pseudosymmetry plane, which contains the U1, U2, O2, Cl1 and Cl5 atoms, with an rms deviation of 0.027 Å. Both uranium atoms are in six-coordinate environments with *fac*-O_3Cl_3 and *cis*-O_2Cl_4 octahedral geometry for U1 and U2, respectively. The five donor atoms of the calixarene define a mean O_5 plane with an rms deviation of 0.155 Å and the uranium atoms are located 1.125(4) (U1) and 1.626(6) Å (U2) from this mean plane. The macrocycle is in the distorted cone conformation, with dihedral angles between the four aromatic rings and the O_5 mean plane of 25.2(2), 87.4(3), 23.3(3), 73.1(3) and 82.9(3)°. These values, with two smaller angles corresponding to aromatic rings almost parallel to the O_5 plane, are analogous to those encountered in compound **1**. The mean values of the U–Cl (terminal) and U–$O_{phenoxy}$ bond lengths of 2.677(16) and 2.14(3) Å, respectively, are comparable to those measured in the other uranium(IV) complexes with calix[*n*]arenes (*n* = 4, 6, 8) previously reported.[1,2] The uranium atoms are further bonded to the bridging chlorine atom Cl1, with a U1–Cl1–U2 angle of 141.13(10)°, and they are at a distance of 5.2862(8) Å from one another. The charge of the trianionic complex is balanced by those of three pyridinium ions hydrogen bonded to three pyridine molecules [N1···N2 2.659(17) Å, N3···N4 2.665(10) Å, N5···N6 2.683(17) Å]. The pyridine molecule (or pyridinium ion) containing N3 is further encapsulated in the calixarene cavity, in which it is held by a π–π stacking interaction with the aromatic ring bearing O4 [centroid···centroid distance 3.69 Å, dihedral angle 13°, centroid offset 0.72 Å].

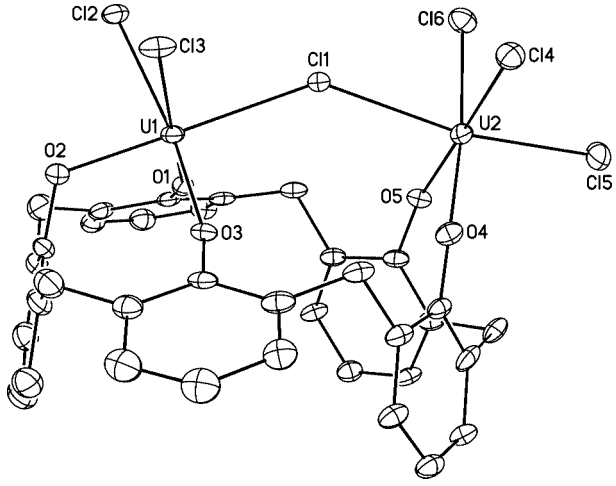

Figure 2. View of the trianion in complex **2**·4py with displacement ellipsoids drawn at the 15% probability level; hydrogen atoms have been omitted.

No reaction was observed between $U(acac)_4$ (acac = MeCOCHCOMe) and calix[5]arene in refluxing THF or pyridine while treatment of $U(acac)_4$ with the sodium salt of the macrocycle led to the sluggish formation of intractable

products. The lesser reactivity of $U(acac)_4$ with respect to UCl_4 was previously noted with the other calix[*n*]arenes (*n* = 4, 6, 8).[1]

Treatment of $U(OTf)_3$ with commercial calix[5]arene gave a mixture of red crystals of **1**·4py and green crystals of the dimeric complex $[U(calix[5]arene–4H)(py)]_2$·4py (**3**·4py). The latter was obtained from the reactions of $U(OTf)_3$ or $U(OTf)_4$ with the thoroughly dried macrocycle but was contaminated with a brown powder of an unidentified compound. Complex **3** could not be isolated in analytical purity because of its insolubility in organic solvents, a problem which was also encountered with most of the uranium(IV) compounds of calix[*n*]arenes (*n* = 4, 6, 8).[1] The formation of **3** from $U(OTf)_3$ implies oxidation of the uranium(III) centre, as in the case of the synthesis of a bis-calixarene U^{IV} complex by treatment of $U(OTf)_3$ with *O*-dimethylated *p-tert*-butylcalix[4]arene.[2] Such oxidation reactions of trivalent uranium complexes by alcohols and phenols were assumed to proceed either by initial proton transfer followed by a valence disproportionation step,[10] or by the direct oxidation of uranium(III) with concomitant evolution of dihydrogen.[11] All the triflate ligands of $U(OTf)_3$ or $U(OTf)_4$ have been substituted by the phenoxide groups of the macrocycle, contrary to the chloride ligands of UCl_4, a difference which has already been noted with the reactions of UX_4 (X = Cl, OTf) and other calixarenes,[1,2] and which reflects the lesser coordinating ability of the triflate ligand.

A view of the centrosymmetric complex **3** is shown in Figure 3. The uranium atom is bound to five oxygen atoms from one calixarene, one oxygen atom from the second (O2′) and the nitrogen atom of the pyridine molecule. The resulting seven-coordinate uranium environment is pentagonal bipyramidal with the N1 and O2′ atoms in apical positions. The uranium atom is located 0.0354(11) Å from the O_5 mean plane defined by the five oxygen atoms of the ligand (rms deviation 0.313 Å) and is thus close to the centre of the O_5 coordination site, like the uranyl ion in the mononuclear complex $[HNEt_3]_2[UO_2$(*p-tert*-butylcalix[5]arene–4H)]. In this respect, complex **3** contrasts with complex **1** and the U^V and U^{VI} complexes with the same stoichiometry previously reported,[4] in which the two metal centres are bound to only two or three phenoxide groups from each calixarene and are located outside the lower rim array. Among the U–O bond lengths, those corresponding to the bridging atom O2 are dissymmetric and larger than the other ones, as well as that associated to atom O5, which is the protonated group (Table 1). The average value for the other bond lengths, 2.19(5) Å, is larger by 0.06 Å than the average value of the $U–O_{phenoxy}$ distances measured in uranium(IV) complexes of calixarenes.[1] Such an increase in the U–O bond length has already been observed in the $[U(Me_2calix)(H_2calix)]$ complex (Me_2calix = *O*-dimethylated *p-tert*-butylcalix[4]arene) and has been attributed to the steric effects generated by the sandwich arrangement.[2] The hydroxy group is involved in a hydrogen bond with the pyridine molecule [O5···N2 2.626(4) Å, O5–H5···N2 157°]. While the uncomplexed calix[5]arene[12] and *p-tert*-butylcalix[5]arene[13] adopt shallow cone conformations, as well as the uranyl complex of *p-tert*-butylcalix[5]arene,[8] the dissymmetric coordination to two metal ions and the presence of an intermolecular hydrogen bond in **3** result in some distortion of the cone geometry; the two phenolic rings associated with metal bridging and hydrogen bonding are more tilted with respect to the O_5 mean plane [dihedral angles 12.5(2), 80.93(8), 15.9(2), 53.26(7) and 72.85(8)° for the rings bearing O1–O5, respectively]. This conformation differs from that encountered in the similar dimeric europium complex $[Eu($*p-tert*-butylcalix[5]arene–3H)$(dmso)_2]_2$, which has been described as a distorted 1,2-partial cone conformation.[7]

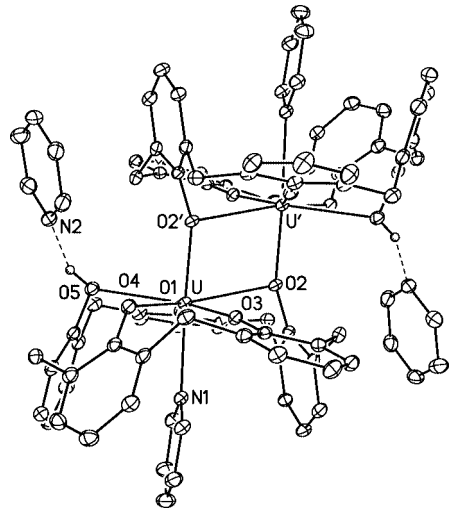

Figure 3. View of complex **3**·4py with displacement ellipsoids drawn at the 30% probability level; two solvent pyridine molecules and hydrogen atoms not involved in hydrogen bonds have been omitted; hydrogen bonds are shown as dashed lines; symmetry code: $2 - x$, $1 - y$, $2 - z$.

Conclusions

Reactions of UCl_4 and $U(OTf)_4$ with calix[5]arene emphasise the extreme sensitivity of uranium(IV) calixarene complexes towards adventitious traces of water and oxygen and their easy oxidation into uranium(V) derivatives. The crystal structure of **2**·4py reveals a novel coordination mode of the calix[5]arene ligand, which was found to be able to accommodate two metal atoms as large as uranium.

Experimental Section

General: All experiments were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were dried by standard methods and distilled immediately before use. The ^1H NMR spectra were recorded with a Bruker DPX 200 instrument and referenced internally using the residual solvent ^1H resonances relative to tetramethylsilane (δ = 0 ppm). Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). Calix[5]arene was purchased from Acros Organics; the TGA-DTA analysis was performed in dry air flow using a SETARAM TGDTA92 analyser; the temperature was increased from ambient to 300 °C applying

heating rates of 10 °C min^{-1}. UCl_4,[14] $U(OTf)_3$ and $U(OTf)_4$[15] were prepared by published methods.

Crystals of $[Hpy]_2[\{U(calix[5]arene–5H)\}_2(\mu_2\text{-}O)]\cdot 4py$ (1·4py): A flask was charged with UCl_4 (7.2 mg, 0.0188 mmol) and commercial calix[5]arene (10 mg, 0.0188 mmol) in pyridine (0.5 mL). The solution immediately turned orange and dark orange crystals of **1**·4py were deposited after 1 d at room temperature (11 mg, 63%).

Synthesis of $[Hpy]_3[U_2(calix[5]arene–5H)Cl_6]\cdot 4py$ (2·4py): Commercial calix[5]arene (50 mg, 0.094 mmol) was dried in pyridine (10 mL) with molecular sieves (4 Å) for 5 d and UCl_4 (71 mg, 0.188 mmol) was then added to the solution. After 5 d at 20 °C, the light green crystals of **2**·4py were filtered off and dried under vacuum (38 mg, 24%). ^{1}H NMR (200 MHz, [D$_5$]pyridine, 23 °C): δ = –0.71 and 0.57 (2×2 H, –CH$_2$–), 1.16 (1 H, –CH$_2$–), 1.27 (2 H, –CH$_2$–), 4.46 (1 H, –CH$_2$–), 4.96 (2 H, –CH$_2$–), 7.43 (1 H, aromatic H), 8.51, 9.70, 11.95, 12.97, 13.22, 15.48 and 16.08 (7×2 H, aromatic H) ppm. The elemental analyses were in agreement with the formula $[Hpy]_3[U_2(calix[5]arene–5H)Cl_6]\cdot 3py$. $C_{65}H_{58}Cl_6N_6O_5U_2$ (1691): calcd. C 45.8, H 3.5, N 4.4; found C 46.1, H 3.4, N 4.3.

Reaction of $U(OTf)_3$ with Calix[5]arene: An NMR tube was charged with $U(OTf)_3$ (12.9 mg, 0.019 mmol) and commercial calix[5]arene (10 mg, 0.019 mmol) in pyridine (0.5 mL). After 12 h at 20 °C, dark orange crystals of **1**·4py and light green crystals of $[U(calix[5]arene–4H)(py)]_2\cdot 4py$ (**3**·4py) were deposited.

Reaction of $U(OTf)_4$ with Calix[5]arene: Commercial calix[5]arene (50 mg, 0.094 mmol) was dried in pyridine (10 mL) with molecular sieves (4 Å) for 5 d and $U(OTf)_4$ (78.7 mg, 0.094 mmol) was then added to the solution. After 5 d at 20 °C, green crystals of **3**·4py contaminated with a brown powder were deposited (35 mg, about 40%). Compound **3**·4py was identified by X-ray diffraction analysis but could not be characterised by ^{1}H NMR because of its insolubility.

X-ray Crystallography: The data 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). The crystals were introduced into glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. The data (φ- and ω-scans)[16] were processed with HKL2000.[17] The structures were solved by direct methods or Patterson map interpretation with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[18] Absorption effects were corrected empirically with the program DELABS in PLATON[19] or with SCALEPACK.[17] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to N1 in **1**·4py and O5 in **3**·4py were found on Fourier-difference maps, but those bound to N atoms in **2**·4py were not found or introduced. All the other hydrogen atoms were introduced at calculated positions. All were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. In **2**·4py, one pyridine molecule (containing N7) was affected with a 0.5 occupancy parameter so as to retain acceptable displacement parameters and four solvent pyridine molecules or pyridinium ions, being badly resolved, were refined as idealised hexagons; restraints on displacement parameters had to be applied for the atoms of some pyridine molecules or pyridinium ions. Crystal data and structure refinement details are given in Table 2. The molecular plots were drawn with SHELXTL.[20]

Table 2. Crystal data and structure refinement details.

	1·4py	**2**·4py	**3**·4py
Empirical formula	$C_{100}H_{82}N_6O_{11}U_2$	$C_{70}H_{63}Cl_6N_7O_5U_2$	$C_{100}H_{82}N_6O_{10}U_2$
M [g mol^{-1}]	2019.78	1771.03	2003.78
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$Pbcn$	$P2_1/c$
a [Å]	15.3242(3)	28.255(2)	13.6891(4)
b [Å]	15.6437(4)	22.0276(13)	16.1392(4)
c [Å]	16.9848(4)	22.5201(10)	18.7131(7)
β [°]	106.932(2)	90	106.4533(12)
V [Å^3]	3895.21(16)	14016.3(14)	3965.0(2)
Z	2	8	2
$\rho_{calcd.}$ [g cm^{-3}]	1.722	1.679	1.678
μ (Mo-K_α) [mm^{-1}]	4.224	4.898	4.148
F(000)	1992	6864	1976
Data collected	25458	212113	128725
Unique data	7300	13221	7524
Observed data[a]	6339	7607	6624
R_{int}	0.045	0.062	0.044
Parameters	538	791	532
R_1	0.025	0.069	0.026
wR_2	0.055	0.199	0.071
S	1.017	0.999	1.039
$\Delta\rho_{min}$ [e Å^{-3}]	–0.62	–1.32	–1.40
$\Delta\rho_{max}$ [e Å^{-3}]	0.89	2.11	1.09

[a] $I > 2\sigma(I)$.

CCDC-610617 and -610619 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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