Calixarene Complexes of Anion-Bridged Oligouranyl Species

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INTRODUCTION

The information available regarding the structural chemistry of calixarene – metal complexes continues to accumulate at a remarkable rate.[1] Focussing in particular on the “parent” macrocycles, that is those that are unsubstituted at the phenolic rim, a particularly broadly investigated family is that of the uranyl-calixarene complexes.[2,3] Examples span ring sizes from calix[4]arene [4] to calix[12]arene [5], and also include thiacalixarenes [4], homooxacalixarenes [6-16], homoazacalixarenes [17-20] and homocalixarenes [21]. One attraction of the uranyl complexes in this context is that they are typically more resistant to hydrolysis when dissolved in noncoordinating solvents under ambient conditions, than the analogous lanthanide or s-block metal complexes. Some common features have emerged from this body of work. For example, the uranyl complexes are often anionic, and the nature of the associated cation can have an impact on the reactivity of the system [22], as well as the resulting structure.[11,19] Complexes of the larger calixarenes are typically oligonuclear, with anions such as oxide, hydroxide, nitrate and carbonate, bridging between the uranyl centres.[2,10] An indication of the growing maturity of the area is that uranyl calixarene complexes are being exploited as components in supramolecular assemblies.[12,13]

Despite this activity, the various factors that control the structure of the uranyl-calixarene complex remain poorly understood in the general case, with apparently subtle changes in reaction conditions and/or structural features resulting in unpredictable alteration of the resulting metal-ligand conglomerate.[2,11] In the absence of reliable structural predictions using, for example, computational techniques, it is necessary to continue to investigate the structural characteristics of these complexes. To this end, we report here a uranyl complex of *p*-t-Bu-calix[6]arene, which in comparison to the two known uranyl complexes of this ligand,[22,23] exemplifies the variations possible in complex structure due to altered reaction conditions. We also report the first uranyl complex of *p*-t-Bu-calix[9]arene, which exhibits some structural features in common with known uranyl calixarene complexes. In both complexes, the uranyl-bridging anion core is, to our knowledge, new to uranyl-calixarene structural chemistry. In a general sense, the present work adds to the structural knowledge concerning U(VI) aryloxides, a field for which there is still quite limited information outside calixarene systems.[24]

EXPERIMENTAL

Synthesis

p-t-Bu-calix[9]arene [25] and *p*-t-Bu-calix[6]arene [26] were synthesised following literature procedures. For simplicity in the following, these are designated calix[9]H_9 and calix[6]H_6 respectively.

$[(HO)\{UO_2(calix[6]H_4)(dmso)\}_3H].\sim 11MeCN.6H_2O$ **1**: Calix[6]H_6 (0.17 g, 0.12 mmol) was slurried in MeCN (4 mL) with triethylamine (24 mg, 0.24 mmol), and the solution heated gently until a clear solution was formed. $[UO_2(dmso)_5](ClO_4)_2$ (0.21 g, 0.24 mmol) in dmso (1 mL) was then added and the solution heated until all the solid dissolved. The solution was filtered and left to stand in a sealed vial until red crystals appropriate for structure determination were deposited.

$(HNEt_3)_3[(OCO_2)(UO_2)_3(calix[9]H_4)].{\sim}6MeCN.H_2O$ **2**: Calix[9]H_9 (0.10 g, 0.12 mmol) was slurried in MeCN (4 mL) and triethylamine was added dropwise until a clear solution was formed. $[UO_2(dmso)_5](ClO_4)_2$ (0.21 g, 0.24 mmol) was then added and the solution heated until all the solid dissolved. The solution was filtered and left to stand until red/brown crystals appropriate for structure determination were deposited.

Structure determinations

General procedure. (Individual variations, difficulties, (etc.) are mentioned for each structure as 'variata'). For the calix[9] compound a full sphere of CCD area detector data was measured at *ca* 153 K (Bruker AXS instrument, ω-scans) yielding $N_{t(otal)}$ data, merging after 'empirical'/multiscan absorption correction (proprietary software) to N unique (R_{int} cited), N_o with $F > 4\sigma(F)$ being considered 'observed' and used in the large block least squares refinement, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ constrained at estimates where possible. For the calix[6] compound a quadrant of data was measured with a single-counter instrument ($2\theta/\theta$ scan mode) and merged after gaussian absorption correction, with a similar refinement protocol, the 'observed' criterion being $I > 3\sigma(I)$. Monochromatic Mo $K\alpha$ radiation sources ($\lambda = 0.7107_3$ Å) were employed. Conventional residuals R ($\Sigma\Delta|F|/\Sigma|F_o|$, R_w $((\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2})$ (weights: $(\sigma^2(F) + 0.0004\ F^2)^{-1}$) are quoted at convergence. Neutral atom complex scattering factors were employed within the context of the Xtal 3.7 program system.[27]˙ Pertinent results are given below and in the Tables and Figures, the latter showing 20% (room temperature), 50% (low temperature) probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Full details are deposited as *.cif* files. A common difficulty with ligands of the present type is rotational disorder within some of the t-butyl groups, such being modelled in terms of a pair of equal or major and minor components summing to unit occupancy. A further common difficulty concerns assignment of the degree of protonation in the presence of very heavy atoms, phenolic proton atoms being estimated as present or otherwise (in the absence of other evidence) as indicated by the magnitude of the relevant O…O spacings. Difference map residues were modelled in terms of solvent, often disordered, as indicated.

Variata. 1**.** **$[(HO)\{UO_2(calix[6]H_4)(dmso)\}_3H]$** ^{t}Butyl 24 was modelled as rotationally disordered over a pair of locations set at equal occupancy after trial refinement, the dmso over a pair of sites, occupancies $x = 2/3$, $1-x$, and MeCN(4-6) about the *3*-axis (non-hydrogen atom displacement parameter forms isotropic). Modelling of the central atom(group) of the aggregate as OH leaves a charge balance problem, one further hydrogen being associated in some undefined manner with the aggregate, the phenolic array being ascribed as associated with four protonic hydrogen atoms. R, R_w for the alternative chirality were 0.070, 0.074.

2. **$(HNEt_3)_3[(OCO_2)(UO_2)_3(calix[9]H_4)]$.** ^{t}Butyl groups 34, 44, 64, 74 were modelled as disordered over equally populated locations, non-hydrogen atom displacement parameter forms isotropic, also true of the (non-disordered) $HNEt_3$(2,3) and MeCN(6) groups, the geometries of the latter being constrained however. The moiety bridging the UO_2 groups was assigned as carbonate.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 250216 for **1**, and 250217 for **2**. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Discussion

Both **1** and **2** were synthesised by dissolution of the appropriate calixarene in acetonitrile with addition of triethylamine, followed by the addition of two equivalents of $[UO_2(dmso)_5](ClO_4)_2$, complexation being indicated by development of the deep red-brown colour of the resulting solution. On standing, crystals of the uranyl complexes were deposited. While crystallisation of the calix[9] complex **2** was found to be insensitive to the presence of excess triethylamine, in the case of the calix[6] system, addition of more than ~2 equivalents of base gave a solution that did not deposit crystals even on prolonged standing. With addition of two equivalents of triethylamine, however, the calix[6] complex **1** was deposited reproducibly from the reaction mixture. Based on the crystal structure determinations, both compounds are presumedly of U(VI), containing that species as the familiar uranyl UO_2^{2+} cation. The O-U-O arrays are all of exemplary linearity (179.2(5) for **1**; 178.5(2), 178.2(2)° for **2**) with U-O ranging between 1.78(1) - 1.813(4) Å.

The array obtained with deprotonated calix[6]H_6 in **1** is trinuclear; the formulation $[(HO)\{UO_2(calix[6]H_4)(dmso)\}_3H]$, presuming a neutral species but without definitive knowledge of the location of all hydrogen atoms, is adopted as consistent with such data as is available. It comprises a triangular array of uranyl uranium atoms, Figure 1, linked in their equatorial planes symmetrically by a 'hydroxyl' oxygen atom, disposed on a crystallographic *3*-axis in cubic space group $P2_13$, and lying 0.65(1) Å out of the U_3 plane so that the OUO uranyl arrays are canted by 19.81(2)° to the U_3 plane, and the oxygen itself pyramidal, consistent with its proposed hydroxy status. Lending further support to the hydroxy assignment, a solvent acetonitrile molecule is situated on the *3*-axis, with the N atom oriented towards the hydroxyl O atom with N...O 2.99(2) Å. While the μ_3-hydroxo bridge is a well known structural motif in general, in U(VI) chemistry other examples of μ_3-O linking three uranyl cations appear to be limited to the oxo anion,[28-34] U-O distances ranging from 2.176 up to 2.286 Å, notably shorter than the 2.41(1) Å in the present case.

The independent uranium atom, in its equatorial plane, is a five-coordinate UO_5 array, *cis*-O-U-O ranging rather widely between 61.6(3) - 82.8(4)° (Table 2). One of the sites is occupied by the dmso oxygen O(0), the others by a pair of adjacent phenoxy-oxygens O(11,21) of the calixarene ligand, O(21) bridging also to a symmetry related uranium. The form of the ligand is that of a rather flattened cone with considerable variation in the tilt of the phenyl rings towards the mean plane; its exact protonation state is uncertain, the precision of the determination not permitting meaningful distinction between the phenoxy C-O distances, which range between 1.38 - 1.42(2), < > 1.395(15) Å. The uncoordinated phenoxy oxygen atoms lie distributed in two pairs, O...O < 3 Å; O(31)...O(41) 2.72(2), O(51)...O(61) 2.72(2) Å, and a hydrogen may reasonably be postulated in association with each pair, with the possibility of a further one in association with O(11)...O(61), 2.67(2) Å; the locations of any others are more mysterious, with possible associations with difference map residues modelled as water molecule oxygens, O(01,02), although these are devoid of any close associations suggestive of hydrogen-bonding.

Two uranyl complexes of *p*-t-Bu-calix[6]arene have been reported previously, $[(UO_2)(calix[6]H_2)]_2(H_3O)_2(HNEt_3)_2$ [23] and $[(UO_2Cl_2)_2(Cs)(calix[6]H_2)](HNEt_3)_3$ [22]. In both these cases, the calixarene interacts with two uranyl cations, and is deprotonated to a greater extent than the example reported here, which is presumably related to the addition of only two equivalents of base in the present system. In all cases, however, the uranyl cation is bound to the calixarene in an "external" manner, with only two phenol O atoms of one calixarene coordinated to any one uranyl cation. It appears that, under conditions investigated to date, this particular calixarene ring size is unable to bind the uranyl cation in an "internal" fashion.[2] The conformations of the calix[6] ligands in all three cases are reasonably described as distorted cones, in terms of the orientations of the phenyl rings, although the two calix[6]H_2 examples have all methylene carbons directed away from the central cavity, [22,23] whereas in the present case, one methylene C atom, C(6) is directed inwards; such a difference is not unexpected given that the ligand is interacting with only one uranyl cation. The conformation in the present case is asymmetric, though there is threefold symmetry for the chiral trimeric complex unit. Within the lattice for the space group found, enantiomeric forms of the trimer must be present in equal numbers.

The metal-containing array in **2** is formulated as achiral, anionic, $[(OCO_2)(UO_2)_2(\text{calix}[9]H_4)]^{3-}$, three residues credibly modelled as 3 x $(HNEt_3)^+$ describing the counterion component, N(10,20) having plausible hydrogen-bonding contacts to uranyl (N(10)...O(2) 2.800(8)) or 'water' molecule (N(20)...O(01) 2.688(10) Å) oxygen atoms. It is interesting to note that the 'water' residue O(01) atom lies *ca.* 3.13 Å from the centroid of ring 9, (Fig 2(b)) consistent with centroid...O distances reported as evidence for π hydrogen bonding in hydrates of sulfonated calix[4]arenes.[35] Also situated in close proximity to the uranyl moieties is an acetonitrile solvent molecule (1), with methyl C...O contacts to uranyl of C(012)...O(4), O(2) 3.19(1), 3.38(1), and phenol O(51) 3.03(1) Å.

The two uranyl groups are found in association with adjacent tridentate fragments of the ligand (Figure 2) U(1) with O(11,21,31); U(2) with O(91,81,71), U-O(11,91) being long (2.490(4), 2.492(4)), U-O(21,81) short (2.164(4), 2.210(4)) and U-O(31,71) intermediate (2.275(4), 2.276(4) Å); O(11)...O(91) is 2.506(5), O(21)...O(31) and O(71)...O(81) 2.962(5), 2.953(6) Å, the sequence involving rings 4, 5, 6 uncoordinated, but disposed in accord with approximate overall *m* symmetry of the anion. The cavity defined by the uncoordinated phenyl rings contains an acetonitrile solvent molecule (2) disposed with the methyl C atom towards the phenyl rings (Figure 2). The two uranium atoms have their five-coordinate equatorial arrays completed each in bidentate fashion by a trifurcating entity modelled as carbonate, O(20) common to both. This coordination mode also occurs in the oligomeric $[(UO_2)_3(CO_3)_6]^{6-}$ anion.[36] The carbonate anion is presumed to have resulted from reaction of adventitious water with CO_2 absorbed into the basic reaction mixture, as has been observed in other metal-calixarene systems.[10,37] A structurally similar array has been reported in the uranyl complex of an acyclic analogue of calix[6]arene, where a nitrate anion, rather than carbonate, bridges between the two uranyl centres.[38] A bridging carbonate is also found in the diuranyl complex of tetrahomodioxacalix[6]arene, but in this case each U atom is bound to one carbonate O atom in an *anti-anti* mode, with a significantly longer U…U distance of 6.69 Å (compared to 4.8238(5) Å in the present case) [10]. In terms of other features of the present structure, O(11)…O(91) is remarkably short (2.506(5) Å), and associated with the longest U-O distances, suggesting the presence of a phenolic hydrogen; O(61)…O(71) and O(31)…O(41) are also notably short (2.717(6), 2.675(6) Å), potential phenolic hydrogen sites. O(41,51,61) have no other nearby oxygen neighbours. U(1,2) lie 0.380(8), 0.471(8) Å out of the CO_3 plane respectively. The conformation of the calixarene ligand differs from that found in the recently reported europium(III) complexes [37]. In the present case, the ligand can be described as a trimeric unit in a cone conformation (rings 4,5,6) linked to a hexameric "pleated loop" configuration (the latter associated with the uranyl cations). In the heptanuclear Eu complex, the calix[9]H_3 ligand assumes a conformation with three trimeric cone-shaped units, each associated with a metal cation. The dinuclear Eu complex is associated with two calix[9]H_6 ligands assuming a comparable, albeit less regular, conformation. Given the differing protonation and coordination states of the calix[9] ligands in each of these complexes, it is difficult to determine the factors dominating the conformational behaviour of this particular calixarene ring size [37].

It is also possible that cation-anion and other lattice interactions (noted above) play some part in influencing the solid state conformations. The triethylammonium groups form bridges between anions involving hydrogen-bonding to uranyl-*O* of one unit and ethyl group inclusion within a cavity of another. The lattice of **2** has a layer structure, with the complexes lying in sheets visible on edge parallel to the *ac* diagonal when the lattice is viewed down *b*.

The present results define two new variations on the theme of calixarenes as cluster keepers [2] and embellish the now quite extensive known range of systems incorporating oligouranyl species. While not even the conformational flexibility of as large a calixarene as calix[9] appears sufficient for the ligand to envelop U(VI) with aryloxide-*O* donors at their optimum distance [3], both calix[6] and calix[9] can be considered as ligands which both restrict the coordination sites at U(VI) available to simple ligands and control the environment (for example, in the sense of whether or not it is chiral) of these sites. Given the recent observation of the first example of η^1-bound CO_2 in a congested uranium complex [39], this indicates that significant applications of uranyl-calixarene complexes may be open to investigation.

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Table 1. Selected crystal refinement data

Compound S	**1**. *ca* 11MeCN.6H_2O	**2**. *ca* 6MeCN. H_2O
	$C_{226}H_{311}N_{11}O_{34}S_3U_3$	$C_{130}H_{189}N_9O_{17}U_2$
M_rDalton	4534.3	2622.0
Crystal system	Cubic	Monoclinic
Space group	$P2_13$ (# 198)	$P2_1/n$
a, Å	29.70(2)	16.043(2)
b, Å		22.728(8)
c, Å		36.357(3)
β, deg,		96.081(2)
V, Å	26198	13182
D_c	1.14_9	1.32_1
Z, f.u.	4	4
μ, cm^{-1}	19.3	25
specimen, mm	0.5 x 0.3 x 0.3	0.45 x 0.40 x 0.05
'T'$_{min,max}$	0.19, 0.39	0.49, 0.71
$2\theta_{max}$, deg.	50	58
N_t	24490	126055
$N(R_{int})$	8169(0.15)	33242(0.06)
N_o	3825	22779
R, R_w	0.054, 0.055	0.054, 0.061

Table 2. The uranium environment, **1**

In this and the subsequent table presented in matrix form, *r* Å is the metal-ligand atom distance, with other entries in the matrix being the angles (deg.) subtended by the relevant atoms at the head of the associated row and column.

	r	O(2)	O(0)	O(11)	O(21)	O(10)	O(21')
O(1)	1.78(1)	179.2(5)	86.6(5)	86.8(4)	93.8(4)	94.0(5)	86.9(4)
O(2)	1.79(1)		94.1(5)	92.4(5)	86.1(4)	85.8(5)	93.9(4)
O(0)	2.41(1)			142.1(4)	62.6(4)	134.8(4)	61.6(3)
O(11)	2.26(1)				80.7(4)	82.8(4)	154.8(4)
O(21)	2.41(1)					161.3(4)	124.1(3)
O(10)	2.37(1)						73.3(4)
O(21')	2.47(1)						

Primed atoms are generated from the asymmetric unit by the transformation *y*, *z*, *x*, i.e. rotation about the *3*-axis passing through the central oxygen atom.

Table 3. Uranium atom environments, **2**

(a) U(1)	*r*	O(2)	O(20)	O(10)	O(11)	O(21)	O(31)
O(1)	1.802(4)	178.5(2)	88.9(2)	91.6(2)	90.7(2)	91.7(2)	89.9(2)
O(2)	1.813(4)		89.8(2)	88.4(2)	88.1(2)	88.9(2)	91.5(2)
O(20)	2.441(4)			53.8(1)	67.5(1)	146.3(1)	130.0(1)
O(10)	2.452(4)				121.1(1)	159.7(1)	76.3(1)
O(11)	2.490(4)					78.8(1)	162.5(1)
O(21)	2.164(4)						83.7(1)
O(31)	2.275(4)						

(b) U(2)	*r*	O(4)	O(20)	O(30)	O(91)	O(81)	O(71)
O(3)	1.788(4)	178.2(2)	88.9(2)	91.1(2)	90.2(2)	91.4(2)	90.2(2)
O(4)	1.792(4)		90.4(2)	89.8(2)	88.0(2)	88.3(2)	91.5(2)
O(20)	2.466(4)			53.5(1)	66.4(1)	146.3(1)	131.4(1)
O(30)	2.460(4)				119.9(1)	160.1(1)	78.0(1)
O(91)	2.492(4)					79.9(1)	162.2(1)
O(81)	2.210(4)						82.3(1)
O(71)	2.276(4)						

Figure captions

Fig. 1 (a) Projection of the $[(HO)\{UO_2(calix[6]H_4)(dmso)_3\}H]$ aggregate of **1** down the *3*-axis passing through the central oxygen atom, and (b) stylised representation of the structure.

Fig. 2 (a) Projection of the anionic $[(OCO_2)(UO_2)_2(calix[9]H_4)]^{5-}$ aggregate of **3**, approximately normal to the carbonate plane, (b) stylised representation in a similar view but from the opposite side of the assembly, including associated $HNEt_3^+$ cations and solvent molecules.

Fig. 1(b)

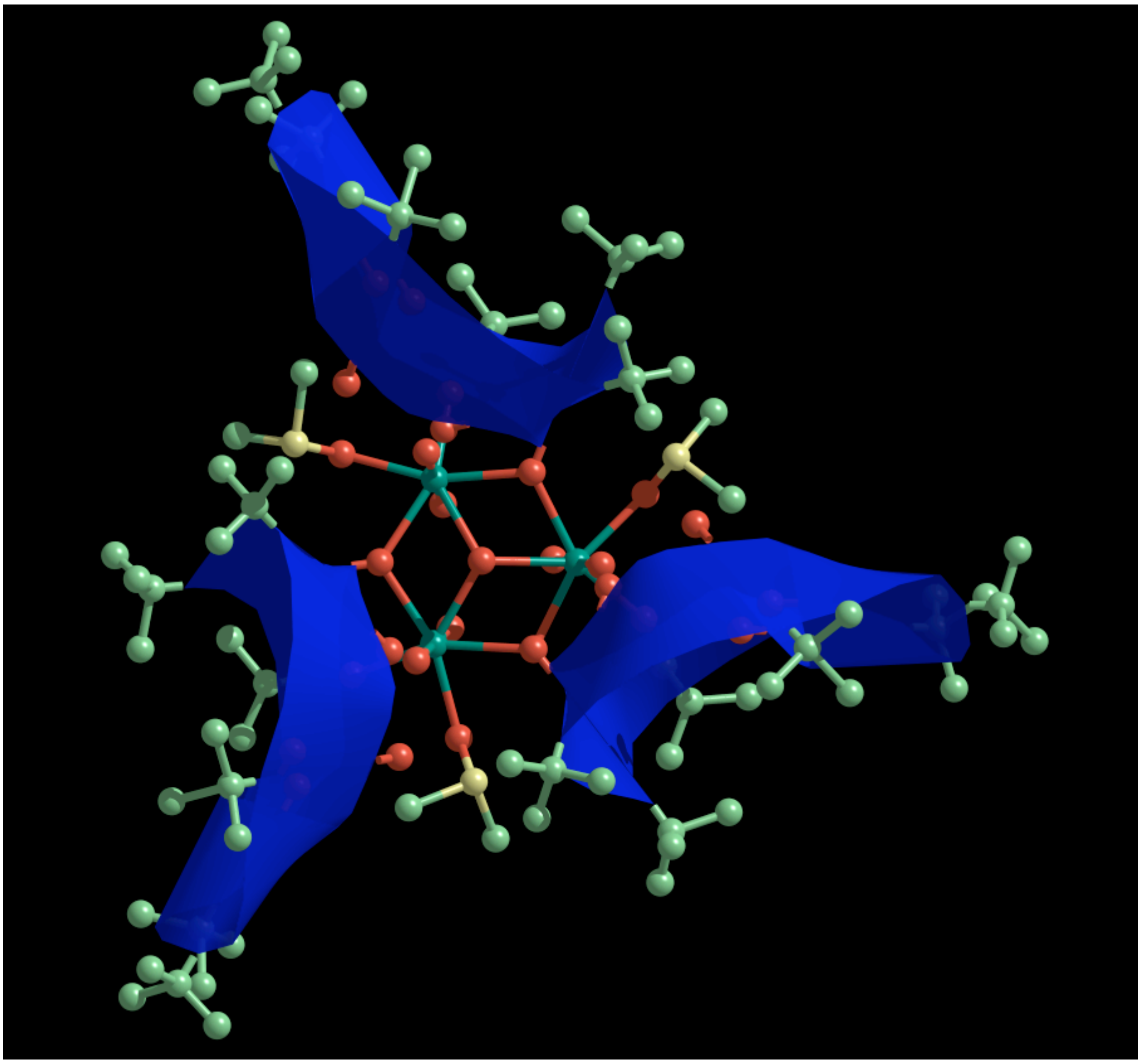

Fig 2(b)