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Synthesis of homooxacalixarenes with 5 and 10 phenol units and crystal structure of their complexes with uranyl ions

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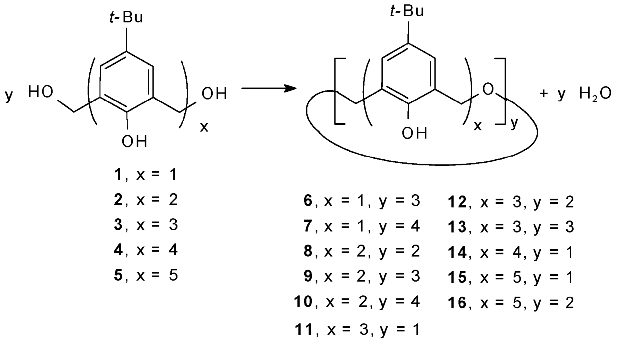
On simply changing the concentration of the reactant, either *p*-*tert*-butyldihomooxacalix[5]arene or *p*-*tert*-butyltetrahomodioxacalix[10]arene can be obtained as the main product in the thermal dehydration of a bishydroxymethylated pentaphenol. The two compounds are suitable for complexation of uranyl ion in the presence of amines, and the X-ray crystal structures of two such complexes are reported. In the complex with *p*-*tert*-butyldihomooxacalix[5]arene, the uranyl ion is sandwiched between two macrocycles, in such a way that each of its two oxo atoms is directed towards the cavity of one homooxacalixarene arranged in a *cone* conformation. On the other hand *p*-*tert*-butyltetrahomodioxacalix[10]arene, in its deca-anionic form, complexes four uranyl ions to give one of the largest species in this family.

Introduction

Homooxacalixarenes[1] are expanded calixarenes in which the CH_2 groups bridging the aromatic units in the typical series are partly or completely replaced by CH_2OCH_2 groups. Few homooxacalixarene systems are currently being investigated, while the family is in principle a very large one and we have made new homooxacalixarenes available both as ether derivatives[2] and as parent phenol compounds.[3,4] In the latter series we are particularly exploiting the thermal dehydration of bishydroxymethylated polyphenol compounds, that was reported many years ago to yield **6**, **8** and **14**,[5] (Scheme 1), but has seldom been employed more recently. We obtained in particular the first large homooxacalixarene systems, namely with six, eight and nine phenol units, through cyclooligomerization of the bishydroxymethylated bisphenol **2**[3] and triphenol **3**.[4]

A fundamental feature of homooxacalixarene with respect to calixarene compounds is that fine tuning of the cavity size, conformational mobility and distance and orientation of the several binding sites in the macrocycle can be operated. The latter point is well illustrated by the variable strength of the complexes between quaternary ammonium ions and the tetramethyl ethers of the five *p*-*tert*-butylhomooxacalix[4]arenes,[2] and by the variety of structures of the uranyl ion complexes with homooxacalix[4]arenes, homooxacalix[6]arenes and homooxacalix[8]arenes.[6]



Scheme 1

The present work was undertaken to fill a gap between the reported macrocycles with 4 and 6 phenol units, namely it reports on the preparation of a homooxacalixarene with 5 phenol units and one CH_2OCH_2 group and of the dimeric homooxacalix[10]arene that formed as well. The two compounds proved to bind uranyl ion in the presence of amine bases and a crystallographic investigation is reported on two of these complexes which we could obtain as single crystals.

Results and discussion

The free ligands

According to Scheme 2, the new homooxacalixarenes **15** and **16** were obtained on dehydrating in xylene at 120 °C the bishydroxymethylated pentaphenol **5**. Compound **15** can be currently designated as a dihomooxacalix[5]arene and **16** as a tetrahomodioxacalix[10]arene, but the alternative names [3.1.1.1.1]homooxacalixarene and [3.1.1.1.1.3.1.1.1.1]homooxacalixarene, respectively, should be preferred to avoid any ambiguity on the relative position of the two CH_2OCH_2 units in **16**.[1]

A very interesting feature of the presently reported dehydration is that on changing the concentration of **5**, either the cyclic monomer or the cyclic dimer can be obtained as the main product, as shown in Fig. 1, in which the observed yields on dehydrating compounds **1–4** are also reported. In all dehydration reactions previously investigated in the series a marked preference was observed for only one of the possible cyclic oligomer products: the cyclic monomer was obtained in the case of **4**,[5] the cyclic dimer was the main product in the case of **2**[3] and **3**,[4] while the cyclic trimer, along with a small amount of the tetramer **7**,[7] formed on dehydrating **1**.† Notwithstanding

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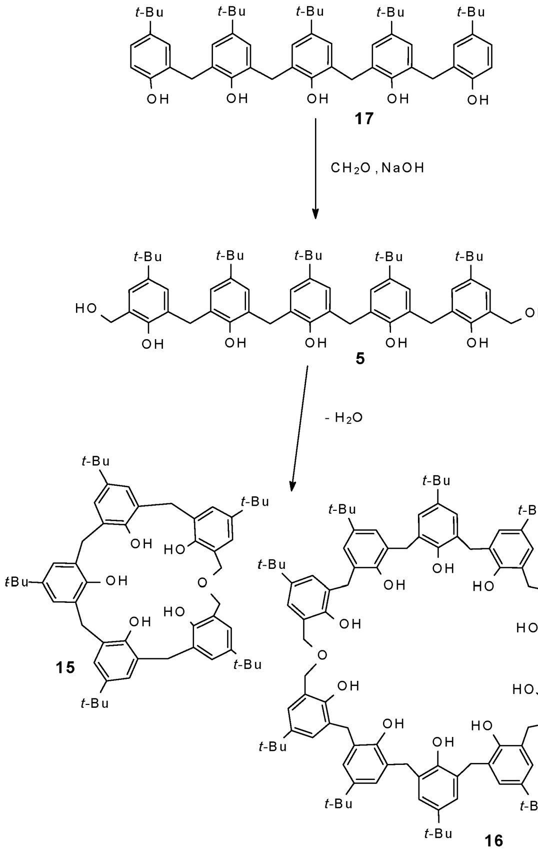
† Values reported for **1** refer to a 0.90 mol dm^{-3} solution in toluene at 120 °C,[8] higher yields have been reported in the presence of *p*-toluenesulfonic acid catalyst.[9]



Scheme 2

the high concentrations used in the dehydration of **1–4**, the smallest non-strained macrocycle apparently formed as the main product in all cases. Actually strains should not be extremely high in the case of **11**, but no evidence was obtained of its formation even at very low concentration of the reactant **3**.[4] The response to substrate concentration is on the other hand a clean-cut one in the case of **5** and on diluting the reactant the main product changes from the dimeric to the monomeric ring.

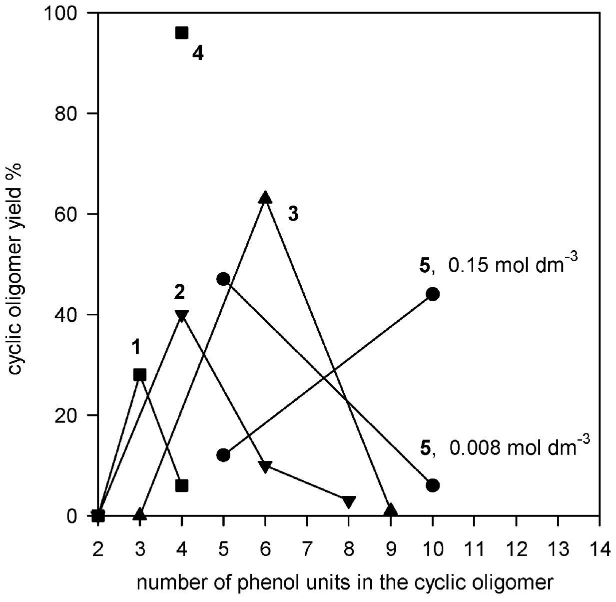


Fig. 1 Yield of cyclic oligomer products on dehydrating compounds **1** (0.75 mol dm^{-3}),[8] **2** (0.75 mol dm^{-3}),[3] **3** (0.25 mol dm^{-3})[4] and **5** (0.15 and 0.008 mol dm^{-3}) in xylene at 120 °C, and **4** (0.25 mol dm^{-3}) in refluxing xylene.[5] The lines simply connect the points for cyclic oligomers formed from a given polyphenol.

In the absence of template and other specific effects, the effective molarity for the formation of a non-strained macrocycle should be about 0.02 mol dm^{-3}.[10] At lower concentration of the bifunctional reactant the intramolecular cyclisation reaction should be favoured with respect to intermolecular reactions, while at significantly higher concentration extensive polymerisation is expected. In the formation of **14** in 96% yield from **4**[5] and in several other cases, intramolecular hydrogen bonds can apparently organise the precursor in a pseudo-cyclic, transition-state-like conformation, thus decreasing the entropy demand for ring closure and promoting cyclisation even at high concentration of the bishydroxymethylated phenol. The latter effect appears to be almost absent in the formation of **15** but relevant in the formation of **16**. Namely the ring closure of the monomeric reactant is not specially favoured and low concentration (0.008 mol dm^{-3}) must be used to obtain **15** in good yields. At high concentration (0.15 mol dm^{-3}) dimerization occurs, but dimers largely react intramolecularly to give **16** rather than intermolecularly to give higher homologues. There was no evidence of the cyclic trimer but it is possible that some formed homooxacalixarenes decompose in the reaction conditions.[3]

Switching the outcome of the reaction from monomeric to dimeric macrocyclic products on simply increasing the reactant concentration is a favourable and rather infrequent occurrence. Interestingly in the present case the addition of an external template[11] for the higher cyclic oligomer is not required, a sort of template action being apparently played by the intramolecular hydrogen bonds.

Crystal structure of the complexes with uranyl ions

Single crystal complexes of both ligands could be obtained on treatment with uranyl nitrate and 1,4-diazabicyclo[2.2.2]octane (DABCO) in pyridine.

The molecular structure of the complex $(HDABCO)_2[UO_2(\mathbf{15}{-}2H)_2]\cdot 3.5C_5H_5N$ (**18**), represented in Fig. 2, provides an unprecedented assemblage among the numerous uranyl complexes with calixarenes and homooxacalixarenes which have been reported.[12] The uranyl ion is sandwiched between two macrocycles, in such a way that each of its two oxygen atoms is directed towards the cavity of one homooxacalixarene. If the finer details of the structure are neglected, the complex has a pseudo-binary axis containing the uranium

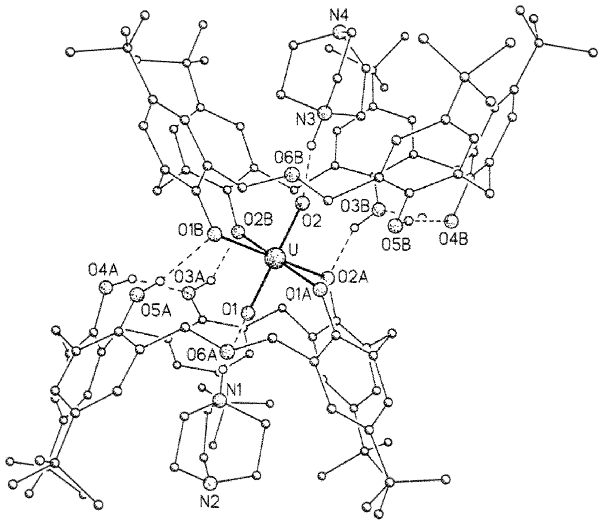


Fig. 2 View of the complex $(HDABCO)_2[UO_2(\mathbf{15}{-}2H)_2]\cdot 3.5C_5H_5N$ (**18**). Hydrogen atoms (except those involved in hydrogen bonds) and solvent molecules are omitted. Carbon atoms have been reduced for clarity. Hydrogen bonds are shown as dashed lines.

Table 1 Environment of the uranium atoms in compounds **18** and **19**: selected bond lengths (Å) and angles (°)

18	U–O1	1.799(6)	O1–U–O2	179.3(4)
	U–O2	1.787(6)	O1A–U–O2A	89.8(3)
	U–O1A	2.238(7)	O2A–U–O2B	84.24(19)
	U–O2A	2.251(7)	O2B–U–O1B	89.0(2)
	U–O1B	2.251(6)	O1B–U–O1A	96.98(19)
	U–O2B	2.243(7)		
19	U1–O1	2.278(17)	O1–U1–O2	76.8(5)
	U1–O2	2.170(14)	O2–U1–O3	80.8(5)
	U1–O3	2.325(14)	O3–U1–O11	81.6(5)
	U1–O7	1.785(17)	O11–U1–O12	54.1(5)
	U1–O8	1.759(15)	O12–U1–O1	66.7(5)
	U1–O11	2.537(16)	O7–U1–O8	175.4(6)
	U1–O12	2.476(15)		
	U2–O4	2.113(13)	O4–U2–O5	82.6(5)
	U2–O5	2.179(15)	O5–U2–O13′	87.3(5)
	U2–O9	1.788(14)	O13′–U2–O13	60.5(6)
	U2–O10	1.801(17)	O13–U2–O11	54.0(5)
	U2–O11	2.523(16)	O11–U2–O4	75.7(5)
	U2–O13	2.491(16)	O9–U2–O10	173.7(8)
	U2–O13′	2.434(13)		
	U1···U2	5.0287(14)	U1···U2′	6.3930(15)
	U2···U2′	4.2549(18)	U1···U1′	10.687(2)

Symmetry code: ′ = 2 − *x*, 2 − *y*, 1 − *z*.

atom and bisecting the segments O1A–O1B and O2A–O2B (approximate C_2 point symmetry). The uranyl ion is bound in its equatorial plane to two phenoxide groups from each macrocycle, with a mean U–O(phenoxide) bond length of 2.246(6) Å, as usual, and the uranium coordination environment is thus distorted square bipyramidal, as often observed in such complexes, with the O1A–U–O1B angle significantly larger and the O2A–U–O2B smaller than the two other angles in the equatorial plane (Table 1). The four phenoxide oxygen atoms define a mean plane with a maximum deviation of 0.004(2) Å, with an out-of-plane displacement of 0.010(2) Å for the uranium atom. The five phenol/phenoxide oxygen atoms of each macrocycle define mean planes with maximum deviations of 0.186(5) and 0.205(5) Å, respectively, the uranium atom being located in between, with out-of-plane displacements of 0.824(4) and 0.839(3) Å, respectively. With respect to each ligand, the uranyl ion is thus only moved by about 0.83 Å from the position which it would occupy if it was complexed in an "internal" fashion and bound to four or five oxygen atoms from the same macrocycle. The dihedral angles between the uranyl mean equatorial plane and the two phenol/phenoxide oxygen mean planes are 29.78(9) and 30.57(10)°, the two macrocycles being tilted due to their bonding to the uranium atom by two adjoining phenoxide groups only (and also slightly offset one with respect to the other). The two protonated DABCO counter-ions are located in the macrocycle cavities and are hydrogen bonded to the uranyl oxo groups (Table 2), as frequently observed. Three out of the five phenolic groups in each ligand retain their proton and both intra- and intermolecular hydrogen bonding ensues. The intramolecular bonds (one in molecule A and two in molecule B) link phenolic groups to each other whereas the three bonds which link molecule A to molecule B involve phenoxide acceptors. The macrocycle adopts a cone conformation, with dihedral angles between the mean plane defined by the five oxygen atoms and the aromatic rings somewhat larger for the coordinated phenoxide groups [63.1(3)–72.5(3), mean value 67(4)°] than for the other ones [41.1(3)–68.8(3), mean value 52(10)°]. The ether oxygen atoms are obviously not coordinated, with distances U···O6A and U···O6B of 4.285(8) and 4.123(8) Å. The ether bridges define *anti* torsion angles [166.6(9)–176.1(9)°] and assume a nearly planar *w* shape.

This structure is of particular interest when compared to those obtained previously with *p*-*tert*-butylcalix[6]arene, since the latter ligand and **15** are comparable in terms of size, notwithstanding the difference in nature of the donor atoms (six phenol groups in *p*-*tert*-butylcalix[6]arene, five phenols and one ether in **15**). We previously used two parameters in order to characterize the calixarene/homooxacalixarene size, which are the sum of the numbers of phenolic units and ether links (*s*), and the number of bonds encircling the central cavity (*m*).[13] Depending on the parameter considered, **15** ($s = 6$, $m = 22$) is equivalent to or intermediate between *p*-R–tetrahomodioxacalix[4]arene ($s = 6$, $m = 20$) and *p*-*tert*-butylcalix[6]arene ($s = 6$, $m = 24$). However, its complexing properties towards the uranyl ion are more akin to those of the latter. *p*-R–Tetrahomodioxacalix[4]arene (R = methyl, *tert*-butyl, phenyl) has been shown to complex one uranyl ion in an "internal" fashion, whatever the deprotonating agent and solvent used.[14] In contrast, all the examples of uranyl complexes with *p*-*tert*-butylcalix[6]arene display "external" coordination,[12] with formation of a sandwich complex with a 2 : 2 metal : ligand stoichiometry in one case.[15] The case of *p*-*tert*-butylcalix[6]arene thus appears very peculiar with respect to its two neighbours in the calixarene series, *p*-*tert*-butylcalix[5]arene, which complexes one uranyl ion "internally"[16] and *p*-R–calix[7]arene, which complexes either one (R = *tert*-butyl)[17] or two (R = benzyl) ions "internally".[18] As discussed elsewhere,[12] this behaviour of *p*-*tert*-butylcalix[6]arene is of importance in the field of "uranophile" design, in which it has often been wrongly supposed that, owing to its six phenolic donor groups, *p*-sulfonatocalix[6]arene was preorganized for uranyl complexation, whereas the calix[6]arene moiety appears particularly maladjusted to complex this ion in a well-defined, "internal" mode. These structural results are also in disagreement with molecular dynamics simulations, which predict "internal" complexation associated with a "five-up, one-down" conformation which has never been observed experimentally.[19] These

Table 2 Hydrogen bonding geometry in compounds **18** and **19**

	D···A/Å		D–H/Å		H···A/Å		D–H···A/°	
18	N1···O1	2.668(13)	N1–H1	0.91	H1···O1	1.79	N1–H1···O1	162
	N3···O2	2.718(10)	N3–H3	1.00	H3···O2	1.81	N3–H3···O2	149
	O3A···O2B	2.710(7)	O3A–H3A	0.96	H3A···O2B	1.83	O3A–H3A···O2B	151
	O4A···O3A	2.734(10)	O4A–H4A	0.91	H4A···O3A	1.91	O4A–H4A···O3A	150
	O5A···O1B	2.766(7)	O5A–H5A	0.77	H5A···O1B	2.02	O5A–H5A···O1B	163
	O3B···O2A	2.697(7)	O3B–H3B	0.92	H3B···O2A	1.85	O3B–H3B···O2A	151
	O4B···O3B	2.720(12)	O4B–H4B	0.89	H4B···O3B	1.91	O4B–H4B···O3B	150
	O5B···O4B	3.196(12)	O5B–H5B	0.96	H5B···O4B	2.26	O5B–H5B···O4B	166
19	N2···O1	2.64(3)	N2–H2	0.91	H2···O1	1.73	N2–H2···O1	175
	N4···O3	2.67(2)	N4–H4	0.91	H4···O3	1.76	N4–H4···O3	179

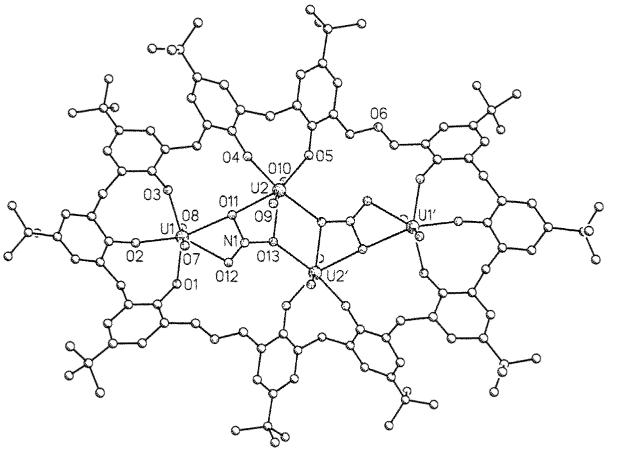


Fig. 3 View of the complex $(HDABCO)_4[(UO_2)_4(\mathbf{16}–10H)(NO_3)_2] \cdot 2DABCO \cdot 6C_5H_5N \cdot 2H_2O$ (**19**). Hydrogen atoms, counter-ions and solvent molecules are omitted for clarity. Symmetry code: ′= 2 − *x*, 2 − *y*, 1 − *z*.

previous observations are strengthened by the present structure of complex **18**, which evidences that, even with one phenolic group replaced by an ether link and flexibility thus increased, calixarenes or homooxacalixarenes with such a size are badly adapted to encompass one uranyl ion. Similarly to *p-tert*-butylcalix[6]arene in the calixarene series, **15** is a peculiar member among homooxacalixarenes, intermediate between *p*-R–tetrahomodioxacalix[4]arene (see above) and *p*-methyloctahomotetraoxacalix[4]arene, which complexes two uranyl ions "internally" (with both phenoxide and ether bonding).[13] As further confirmation of this trend, we obtained another uranyl complex with **15**, in the presence of triethylamine, which is a 2 : 2 sandwich species similar to one of the *p-tert*-butylcalix[6]arene complexes,[15] but no complete crystallographic characterization was possible due to the very low crystal quality.

In the presence of DABCO, **16**, in its deca-anionic form, complexes four uranyl ions to give one of the largest species in this family, $(HDABCO)_4[(UO_2)_4(\mathbf{16}–10H)(NO_3)_2] \cdot 2DABCO \cdot 6C_5H_5N \cdot 2H_2O$ (**19**). As evidenced in Fig. 3, this complex is centrosymmetric and the complexed moiety is in fact the hexacation $[(UO_2)_4(NO_3)_2]^{6+}$ in which each nitrate ion acts as a bidentate, chelating ligand towards two uranyl ions and as a monodentate ligand towards another. The uranium atom U1 is bound, in its equatorial plane, to three phenoxide groups and two nitrate oxygen atoms whereas U2 is bound to two phenoxides and three nitrate oxygens, both uranium atoms thus being in pentagonal bipyramidal environments. The mean U–O(phenoxide) and U–O(nitrate) bond lengths, 2.21(9) and 2.49(4) Å (including both uranium atoms), respectively, are in the usual ranges, the small variations in U–O(phenoxide) bond lengths likely to be due to the impossibility for the ligand to perfectly match the ideal geometry around each of the four cations. The mean equatorial planes defined by the five donor atoms around each uranyl ion have maximum deviations of 0.02(1) and 0.06(1) Å and the out-of-plane displacements of U1 and U2 are 0.015(7) and 0.010(7) Å, respectively. The dihedral angle between these two planes is 13.4(6)°. The homooxacalixarene, which assumes a rather flat shape (Fig. 4), can be viewed as built from two subunits related by the symmetry centre, separated by the O6–O6′ line and containing two uranyl ions and one nitrate ion each. These two halves are connected by the bridging nitrate oxygen atoms O13 and O13′. In each subunit, the torsion angles defined by the four methylene links can be used to define the conformation.[20] Notwithstanding rather large variations with respect to the ideal *gauche* value, since they are in the range 41(3)–125(2)°, these angles define a sequence (+−, −+, +−, −+) typical of a "pleated" or "undulated loop" arrangement frequent in large calixarenes (for example calix[10]arene[21]), albeit much distorted in the present case. It may be noted that complex **19**, as well as the tetranuclear uranyl complex obtained with *p-tert*-butylcalix[12]arene,[22] contain the same $[(UO_2)_2NO_3]^{3+}$ moiety which is found in the binuclear complex of an acyclic *p-tert*-butylhexaphenol,[23] with one of the six oxygen donor atoms in the latter replaced by a bridging nitrate oxygen in **19** and a pyridine molecule in the *p-tert*-butylcalix[12]arene complex. The two ether bridges in **19** define *anti* torsion angles [177(2) and 162(2)°], which give them the usual *w* shape. The HDABCO cations are located on either side of the mean plane of the molecule and they are hydrogen bonded to the phenoxide oxygen atoms O1 and O3.

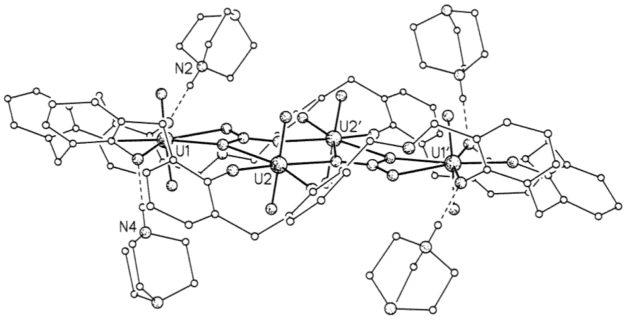


Fig. 4 View of the complex $(HDABCO)_4[(UO_2)_4(\mathbf{16}–10H)(NO_3)_2] \cdot 2DABCO \cdot 6C_5H_5N \cdot 2H_2O$ (**19**). Hydrogen atoms (except those involved in hydrogen bonds), *tert*-butyl groups and solvent molecules are omitted. Carbon atoms have been reduced for clarity. Hydrogen bonds are shown as dashed lines. Symmetry code: ′ = 2 − *x*, 2 − *y*, 1 − *z*.

We have previously reported the crystal structures of two tetra-uranate complexes with *p-tert*-butyloctahomotetraoxacalix[8]arene,[13,24] the size of which (s = 12, m = 40) is slightly smaller than that of **16** (s = 12, m = 44). This is the reason why the tetra-uranate core in complex **19** is less tightly packed than those in the *p-tert*-butyloctahomotetraoxacalix[8]arene complexes, the nitrate bridging species in the former being replaced by water/hydroxo/oxo species in the latter. The overall shapes of the complexes are also different, since *p-tert*-butyloctahomotetraoxacalix[8]arene has to match a square or an oblong tetra-uranate core whereas **16** encompasses an elongated cluster and adopts a shape adapted in consequence, with distances O5···O5′ and O2···O2′ of 7.38(3) and 15.00(3) Å, respectively. *p-tert*-Butylcalix[12]arene, which is even larger (s = 12, m = 48) has been reported to complex two independent $[(UO_2)_2NO_3(py)]^{3+}$ moieties,[22] but it could possibly yield a higher nuclearity assemblage, should pyridine be avoided, since replacement of this coordinating solvent by less bulky oxo or hydroxo bridges could leave sufficient space for the encapsulation of a larger number of uranyl ions. A common feature of many polyuranate complexes of large calixarenes or homooxacalixarenes is to include nearly planar polymetallic clusters, which is due to the peculiar geometric requirements of the uranyl ion, whereas much more "three-dimensional" assemblages have been reported in the case of rare-earth cations.[25]

Experimental

Synthesis

^1H NMR and ^{13}C NMR spectra were taken in $CDCl_3$ at 298 K on a Bruker AC 300 spectrometer, using TMS as an internal standard. Mass spectra were obtained with a Fisons Instruments VG-Platform Benchtop LC-MS (negative ion electrospray mass spectra, (ES^-) MS; flow injection analysis in MeOH of samples in MeOH–MeONa). Melting points (uncorrected) were obtained in sealed evacuated capillaries. Column chromatography was carried out on 230–400 mesh silica gel (Merck).

4-*tert*-Butyl-2,6-bis-[5-*tert*-butyl-3-(5-*tert*-butyl-2-hydroxy-3-hydroxymethyl-benzyl)-2-hydroxy-benzyl]-phenol (5). A mixture of **17**[26] (12.0 g, 15.0 mmol), 37% CH_2O (44 ml), 25% NaOH (11.2 ml), dioxane (32 ml) and MeOH (60 ml) was heated at 55 °C for 60 h. After cooling, a white solid was collected by filtration, washed with a mixture of MeOH (10 ml), H_2O (7 ml) and dioxane (4 ml), diluted with water, neutralized with 1N HCl and extracted in ether. Solvent evaporation gave practically pure **5**, 9.60 g, 75% yield. An analytically pure sample was obtained from $CHCl_3$–hexane: mp 206–208 °C; MS (ES^-) m/z 858 $[M - H]^-$, 880 $[M - 2H + Na]^-$, 902 $[M - 3H + 2Na]^-$; ^1H NMR $\delta = 1.24$ (s, 18H, *t*-Bu), 1.24 (s, 18H, *t*-Bu), 1.25 (s, 9H, *t*-Bu), 3.29 (s, 2H, $ArCH_2OH$), 3.84 (s, 4H, $ArCH_2Ar$), 3.86 (s, 4H, $ArCH_2Ar$), 4.83 (s, 4H, $ArCH_2OH$), 6.94 (d, $J = 2.0$ Hz, 2H, Ar*H*), 7.12 (s, 4H, Ar*H*), 7.14 (s, 2H, Ar*H*), 7.21 (d, $J = 2.0$ Hz, 2H, Ar*H*), 9.20 (s, 2H, ArO*H*), 9.38 (s, 2H, ArO*H*), 9.41 (s, 1H, ArO*H*). ^{13}C NMR $\delta = 31.5$, 31.6, 32.2, 34.0, 34.0, 64.6, 123.4, 125.0, 125.8, 125.8, 125.9, 127.0, 127.1, 127.2, 127.2, 143.5, 144.1, 144.2, 147.2, 147.3. Calc. for $C_{56}H_{74}O_7$: C, 79.15; H, 8.69; found: C, 79.00; H, 8.41.

7,13,19,25,31-penta-*tert*-butyl-33,34,35,36,37-pentahydroxy-2,3-dihomo-3-oxacalix[5]arene (15). A mixture of **5** (1.51 g, 1.76 mmol) and xylene (210 ml) was carefully nitrogen flushed, then stirred and heated at 120 °C under a nitrogen atmosphere during 5 h. Most xylene was evaporated under vacuum and from the residue (5 ml) a white solid was collected by filtration. This proved to be **16** (80 mg, 6% yield). The filtrate was subjected to column chromatography (eluent: toluene) to give pure **15** (700 mg, 47% yield): mp 197–199 °C (from $CHCl_3$–MeOH); MS (ES^-) m/z 840 $[M - H]^-$, 862 $[M - 2H + Na]^-$, 419 $[M - 2H]^{2-}$; ^1H NMR $\delta = 1.26$ (s, 18H, *t*-Bu), 1.27 (s, 18H, *t*-Bu), 1.29 (s, 9H, *t*-Bu), 3.73 (s, 4H, $ArCH_2Ar$), 4.00 (s, 4H, $ArCH_2Ar$), 4.78 (s, 4H, $ArCH_2O$), 6.97 (d, $J = 2.0$ Hz, 2H, Ar*H*), 7.09 (d, $J = 2.4$ Hz, 2H, Ar*H*), 7.12 (s, 2H, Ar*H*), 7.21 (d, $J = 2.4$ Hz, 2H, Ar*H*), 7.23 (d, $J = 2.0$ Hz, 2H, Ar*H*), 9.38 (s, 2H, ArO*H*), 9.59 (s, 2H, ArO*H*), 10.19 (s, 1H, ArO*H*). ^{13}C NMR $\delta = 31.5$, 31.5, 31.6, 32.0, 33.1, 34.0, 34.0, 73.1, 122.1, 124.6, 125.8, 126.1, 126.2, 126.3, 126.4, 126.5, 127.4, 127.9, 143.2, 143.5, 144.1, 147.6, 148.5, 150.0. Calc. for $C_{56}H_{72}O_6$: C, 79.96; H, 8.63; found: C, 79.70; H, 8.86.

7,13,19,25,31,39,45,51,57,63-deca-*tert*-butyl-65,66,67,68,69,70,71,72,73,74-decahydroxy-2,3,34,35-tetrahomo-3,35-dioxacalix[10]arene (16). A mixture of **5** (500 mg, 0.58 mmol) and xylene (3.5 ml) was flushed and reacted as reported for **15**. The cooled and filtered reaction mixture was chomatographed as above to give **15** (60 mg, 12% yield) while the recovered white solid was washed with toluene and with acetone to give pure **16** (215 mg, 44% yield): mp 212–214 °C; MS (ES^-) m/z 1680 $[M - H]^-$, 1702 $[M - 2H + Na]^-$, 840 $[M - 2H]^{2-}$; ^1H NMR $\delta = 1.22$ (s, 18H, *t*-Bu), 1.25 (s, 36H, *t*-Bu), 1.27 (s, 36H, *t*-Bu), 3.88 (s, 16H, $ArCH_2Ar$), 4.66 (s, 8H, $ArCH_2O$), 6.98 (d, $J = 2.5$ Hz, 4H, Ar*H*), 7.01 (s, 4H, Ar*H*), 7.05 (d, $J = 2.5$ Hz, 4H, Ar*H*), 7.15, (d, $J = 2.5$ Hz, 4H, Ar*H*), 7.30 (d, $J = 2.5$ Hz, 4H, Ar*H*), 8.85–9.05 (m, 10H, ArO*H*). ^{13}C NMR $\delta = 31.5$, 31.6, 31.9, 32.9, 34.0, 34.0, 34.0, 71.8, 122.7, 124.7, 125.2, 125.8, 126.0, 126.4, 127.0, 127.7, 127.8, 143.1, 143.6, 144.0, 147.5, 148.4, 150.3. Calc. for $C_{112}H_{144}O_{12}$: C, 79.96; H, 8.63; found: C, 79.61; H, 8.48.

$(HDABCO)_2[UO_2(15{-}2H)_2] \cdot 3.5C_5H_5N$ (18). Compound **15** (10 mg, 0.012 mmol) and a large excess of 1,4-diazabicyclo[2.2.2]octane, DABCO (20 mg, 0.18 mmol) were dissolved in $CHCl_3$ (50 ml). A two-fold excess of uranyl nitrate hexahydrate (12 mg, 0.024 mmol) in CH_3OH (15 ml) was then added dropwise and the resulting light orange solution was refluxed for 15 min. The product was then evaporated to dryness, dissolved in pyridine and the solution allowed to slowly evaporate, finally depositing dark orange crystals suitable for X-ray crystallography. The included pyridine appeared to be easily lost, the composition of a partly dried sample being close to that calculated for $(HDABCO)_2[UO_2(\mathbf{15}{-}2H)_2] \cdot 2C_5H_5N$. Calc. for $C_{134}H_{176}N_6O_{14}U$: C, 68.99; H, 7.60, N, 3.60; found: C, 68.69; H, 7.95, N, 3.45. ^1H NMR spectra indicated that the free ligand was present as the main component in $CDCl_3$ solution.

$(HDABCO)_4[(UO_2)_4(16{-}10H)(NO_3)_2] \cdot 2DABCO \cdot 6C_5H_5N \cdot 2H_2O$ (19). Compound **16** (17 mg, 0.010 mmol) was dissolved under reflux in $CHCl_3$ (100 ml) in the presence of an excess of DABCO slightly larger than ten-fold (15 mg, 0.13 mmol). A six-fold excess of uranyl nitrate hexahydrate (30 mg, 0.060 mmol) in CH_3OH (20 ml) was then added dropwise and the resulting dark orange solution was refluxed for 5 min. The product was then evaporated to dryness, dissolved in pyridine and the solution allowed to slowly evaporate over about three weeks, finally depositing dark orange crystals suitable for X-ray crystallography. The included pyridine appeared to be easily lost, the composition of a partly dried sample being close to that calculated for $(HDABCO)_4[(UO_2)_4(\mathbf{16}{-}10H)(NO_3)_2] \cdot 2DABCO \cdot 4C_5H_5N \cdot 2H_2O$. Calc. for $C_{168}H_{234}N_{18}O_{28}U_4$: C, 51.66; H, 6.04, N, 6.45; found: C, 51.30; H, 6.32, N, 6.78. ^1H NMR spectra in $CDCl_3$ solution were hardly interpretable due to the presence of several broad signals.

Crystallography

The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[27] using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystals were introduced in Lindemann glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from the reflections collected on ten frames and were then refined on all data. The data were processed with DENZO-SMN.[28] The structures were solved by Patterson map interpretation (**18**) or by direct methods (**19**) with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[29] Absorption effects were empirically corrected with the program DELABS from PLATON.[30] All non-hydrogen atoms were refined with anisotropic displacement parameters. Some restraints on bond lengths and/or displacement parameters

Table 3 Crystal data and structure refinement details

	18	**19**
Empirical formula	$C_{141.5}H_{183.5}N_{7.5}O_{14}U$	$C_{178}H_{244}N_{20}O_{28}U_4$
M/g mol^{-1}	2451.49	4064.05
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	16.0169(17)	13.4500(14)
b/Å	16.2046(10)	19.1428(16)
c/Å	27.024(3)	20.2899(18)
α/°	96.325(6)	117.130(6)
β/°	96.207(5)	102.485(7)
γ/°	108.071(6)	96.117(7)
V/Å^3	6552.0(11)	4411.0(7)
Z	2	1
μ/mm^{-1}	1.302	3.734
Reflections collected	39820	23830
Independent reflections	21721	14405
Obsd. reflections $[I > 2\sigma(I)]$	11742	4660
R_{int}	0.083	0.092
Parameters refined	1522	1049
R_1	0.087	0.089
wR_2	0.184	0.159

have been applied for some *tert*-butyl groups, the water molecule and some parts of DABCO and pyridine molecules. In compound **18**, one pyridine molecule was modelled with a 0.5 occupancy factor so as to keep an acceptable displacement parameter. The hydrogen atoms bound to nitrogen and oxygen atoms in **18** were found on a Fourier-difference map. The other hydrogen atoms in both compounds were introduced at calculated positions, except those of the water molecule in compound **19**. All were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (OH, NH, CH, CH_2) or 1.5 (CH_3) times that of the parent atom. Crystal data and structure refinement parameters are given in Table 3.‡ The molecular plots were drawn with SHELXTL.[31] All calculations were performed on a Silicon Graphics R5000 workstation.

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