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## Supramolecular Chemistry

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### A Bis(*p-tert*-butyloctahomotetraoxacalix[8]arene) Capsule with [(UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub>] Links and a Disordered [Rb<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>] Inner Core

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# A Bis(*p*-*tert*-butyloctahomotetraoxacalix[8]arene) Capsule with [(UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub>] Links and a Disordered [Rb<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>] Inner Core

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*p*-*tert*-Butyloctahomotetraoxacalix[8]arene (LH<sub>8</sub>) reacts with uranyl nitrate hexahydrate in the presence of rubidium hydroxide to give a mixed complex that can be viewed as a tetrauranate dimer [(UO<sub>2</sub>)<sub>4</sub>(LH<sub>4</sub>)<sub>2</sub>(OH)<sub>4</sub>] containing four disordered rubidium ions and water molecules. Two uranyl ions are complexed in an "external" fashion by each macrocycle, each of them bound to two phenoxide groups and one ether group, as well as to two bridging hydroxide ions. The latter ensure the formation of a dimeric capsule that contains the disordered set of alkali metal ions. Apart from water molecules, the Rb<sup>+</sup> ions are bound to the uranyl oxo groups directed towards the inner cavity, and to phenol and ether oxygen atoms from the macrocycle. The resulting octanuclear complex presents an unprecedented geometry evidencing the assembling potential of uranyl ions.

**Keywords:** Uranyl ion; Rubidium ion; Calixarene; Homooxacalixarene; Crystal structure

## INTRODUCTION

Important advances have been made recently in the synthesis of large calixarenes [1] and homooxacalixarenes [2]. Despite the difficulties encountered in growing single crystals of these very flexible compounds, the knowledge of their structural features is progressing and the extremely unusual crystal structure of the very large *p*-*tert*-butylcalix[16]arene has even been reported [3]. Numerous complexes of *p*-*R*-calix[8]arene with alkali metal, transition metal, lanthanide and actinide ions have

been investigated in the solid state but, to the best of our knowledge, the uranyl ion is the only metal cation for which several complexes of larger calixarenes and homooxacalixarenes have been obtained and characterized [4]. Among the largest species obtained with this cation, we have described the crystal structure of the tetranuclear complex of *p*-*tert*-butyloctahomotetraoxacalix[8]arene [5], in which the macrocycle is octa-anionic. In the cases in which the uranyl ion is complexed in an "internal" fashion, that is located inside the calixarene and with the calixarene mean plane close to its equatorial plane, the nuclearity of the resulting species can be predicted simply from the macrocycle size [5], the large calixarenes and homooxacalixarenes having a marked propensity to complex polyuranate clusters with various additional bridges, such as water molecules or hydroxide, nitrate or carbonate ions. These uranyl complexes are generally obtained in the presence of organic, nitrogen-containing, bases. Alkali metal-containing bases can also be used as deprotonating agents for calixarenes or homooxacalixarenes, resulting in the formation of alkali metal complexes, which have recently been the subject of much attention [6–8]. In order to extend this study of alkali metal ion complexation to novel systems, we began an investigation of the synthesis and crystal structures of mixed uranyl/alkali metal ion complexes of homooxacalixarenes. The interest in such work is increased by the fact that it provides information both on the coordination of alkali metal ions by systems in which phenolic oxygens compete with aromatic rings and ether or oxo groups

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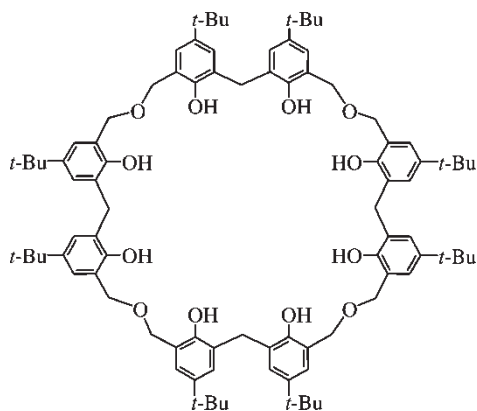


FIGURE 1 *p*-*tert*-Butyloctahomotetraoxacalix[8]arene (LH<sub>8</sub>).

as ligating sites and on the effect of the replacement of amine bases by hydroxides on uranyl bonding and the resulting supramolecular structure. We have recently reported our initial results obtained with *p*-*tert*-butyltetrahomodioxacalix[4]arene and alkali metal hydroxides [9]. Depending on the alkali metal ion size and "hardness" and the resulting preference for oxygen- or aromatic polyhapto-coordination, various arrangements, either monomeric (Li<sup>+</sup>), dimeric (Na<sup>+</sup>) or polymeric (K<sup>+</sup>, Cs<sup>+</sup>), are obtained, all of them including the same UO<sub>2</sub>/homooxacalixarene core. The novelty of these results led us to undertake an analogous investigation with larger homooxacalixarenes, for which less simple results are expected due to the higher flexibility and versatility of the macrocycle. As part of this study, we report herein the results obtained with a very large macrocycle, *p*-*tert*-butyloctahomotetraoxacalix[8]arene, denoted LH<sub>8</sub> hereafter (Fig. 1), for which only Rb<sup>+</sup> in the Li<sup>+</sup>–Cs<sup>+</sup> series could be used to grow single crystals of suitable quality.

## EXPERIMENTAL

### Synthesis

The ligand *p*-*tert*-butyloctahomotetraoxacalix[8]arene (LH<sub>8</sub>) was synthesized as reported previously [10].

#### $[(UO_2)_4Rb_4(LH_4)_2(OH)_4(H_2O)_4] \cdot 12C_5H_5N$ (**1**)

LH<sub>8</sub> (16 mg, 0.011 mmol) and RbOH·H<sub>2</sub>O (11 mg, 0.092 mmol) were refluxed in chloroform (100 ml). Uranyl nitrate hexahydrate (28 mg, 0.056 mmol) in methanol (20 ml) was added dropwise, resulting in an orange solution that was refluxed for 5 min. The resulting powder was dissolved in pyridine, yielding orange single crystals suitable for X-ray crystallography on slow evaporation. It should be noted that pyridine is mainly present in the compound as a solvent. Compound **1** is scarcely soluble in

CDCl<sub>3</sub> and the only clear signals in the <sup>1</sup>H NMR spectrum are those of the free ligand.

When the same experiment is carried out in the presence of lithium, sodium, potassium or caesium hydroxides, orange solutions are also obtained, indicating that uranyl complexation occurs as well. However, the investigation of such large and flexible macrocycles, often highly solvated and disordered, is often limited by the crystallization step and, in the present case, it was only with Li<sup>+</sup> that very poorly diffracting crystals could be obtained, giving a very rough structural model at best, which will only be briefly alluded to for the sake of comparison with compound **1**.

### Crystallography

The data for compound **1** were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer [11] using graphite-monochromated MoK $\alpha$  radiation (0.71073 Å). The crystal (0.25 × 0.10 × 0.08 mm<sup>3</sup>) was introduced in a Lindemann glass capillary with a protecting "Paratone" oil (Exxon Chemical Ltd.) coating. The unit cell parameters were determined from the reflections collected on 10 frames and were then refined on all data. The data were processed with DENZO-SMN [12]. The structure was solved by direct methods with SHELXS-97 [13] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on *F*<sup>2</sup> with SHELXL-97 [13]. Absorption effects were empirically corrected with the program DELABS from PLATON [14]. The structure was solved in the tetragonal space group *P*4/*nnc* with much disorder on the rubidium atoms. All attempts to solve it in lower symmetry space groups (tetragonal or orthorhombic) were unsuccessful. The rubidium atom was found to be disordered over three positions that were refined with occupancy parameters constrained to sum to unity. One *tert*-butyl group was also found to be rotationally disordered over two positions that were also refined with occupancy parameters constrained to sum to unity. The disordered water molecules (one of them on a special position) were affected with occupancy parameters taking into account their association with one of the three positions of the rubidium atom. Three solvent pyridine molecules were affected by a 0.5 occupancy factor so as to keep a physically significant displacement factor. Another one was disordered around a binary axis. Some restraints on bond lengths and/or displacement parameters were applied for some *tert*-butyl groups and pyridine and water molecules. All non-hydrogen atoms were refined with anisotropic displacement parameters, except those of the disordered *tert*-butyl group. The hydrogen atoms bound to the phenolic oxygen atoms were found on a Fourier-difference map and

all the others (except those of the water molecules and those of the disordered *tert*-butyl group and pyridine molecules) were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (OH, CH, CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times that of the parent atom. Some voids in the lattice indicate the presence of other, unresolved, solvent molecules. The molecular plots were drawn with SHELXTL [15]. All calculations were performed on a Silicon Graphics R5000 workstation.

#### Crystal Data and Refinement Details

[(UO<sub>2</sub>)<sub>4</sub>Rb<sub>4</sub>(LH<sub>4</sub>)<sub>2</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]<sub>2</sub>·12C<sub>5</sub>H<sub>5</sub>N (**1**) C<sub>244</sub>H<sub>304</sub>N<sub>12</sub>O<sub>40</sub>Rb<sub>4</sub>U<sub>4</sub>, *M* = 5338.99, tetragonal, space group *P4/mnc*, *a* = *b* = 31.843(3), *c* = 28.4362(15) Å, *V* = 28834(4) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.230 g cm<sup>-3</sup>, *μ* = 2.970 mm<sup>-1</sup>, *F*(000) = 10752. Refinement of 750 parameters on 12 983 independent reflections out of 131 059 measured reflections (*R*<sub>int</sub> = 0.089) led to *R*<sub>1</sub> = 0.082, *wR*<sub>2</sub> = 0.160 and *S* = 0.94.

Crystallographic data for the structural analysis of compound **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 204439. 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).

## RESULTS AND DISCUSSION

In the presence of triethylamine as a deprotonating agent, the ligand LH<sub>8</sub> gives the tetranuclear uranyl complex [HNEt<sub>3</sub>]<sub>2</sub>[(UO<sub>2</sub>)<sub>4</sub>(L)(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sub>1.5</sub>·NEt<sub>3</sub>·2.5H<sub>2</sub>O·CH<sub>3</sub>OH **2** [5], in which all the phenolic protons have been removed, resulting in octaphenoxide coordination of the central [(UO<sub>2</sub>)<sub>4</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] polyuranate cluster (each uranyl ion being bound to two methylene-linked phenoxide groups). Replacement of NEt<sub>3</sub> by RbOH during complex synthesis results in a completely different and much more complicated structure (Fig. 2). The asymmetric unit in [(UO<sub>2</sub>)<sub>4</sub>Rb<sub>4</sub>(LH<sub>4</sub>)<sub>2</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]<sub>2</sub>·12C<sub>5</sub>H<sub>5</sub>N **1** corresponds to a quarter of the complete complex molecule, that is to half a homooxocalixarene molecule. The second half of the molecule is deduced from the first through the binary axis in (0.25, 0.25, *z*), whereas the second macrocycle in the dimer is related to the first by the binary axis in (*x*, 0.25, 0.25). There are only two uranyl ions per calixarene and these are not bound in an "internal" fashion as in compound **2**, but in an "external" mode, the uranyl axis being roughly parallel to the mean macrocycle

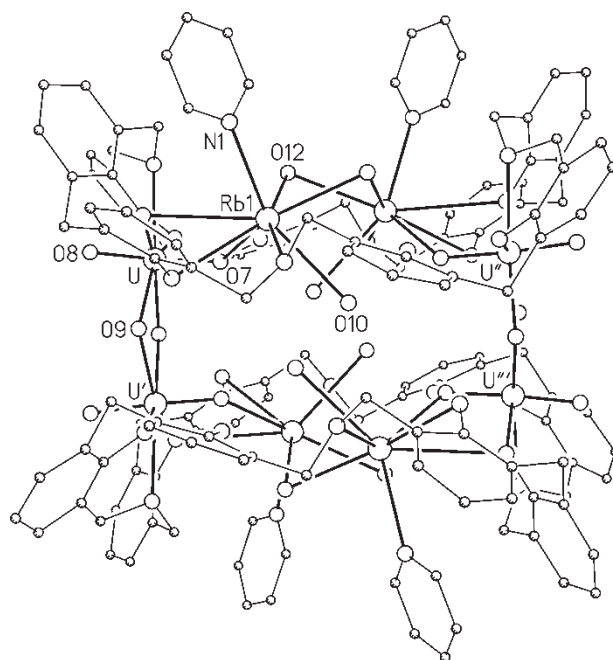


FIGURE 2 View of the complex molecule in **1**. Only one out of the three rubidium positions and its symmetry-related equivalents are represented. The calixarene skeleton is represented by thin lines and the carbon atoms by small spheres for clarity. *tert*-Butyl groups, hydrogen atoms and solvent molecules are omitted. Symmetry codes: ' = *x*, 0.5 - *y*, 1.5 - *z*;'' = 1.5 - *x*, 0.5 - *y*, *z*;''' = 1.5 - *x*, *y*, 1.5 - *z*.

plane. Each uranyl ion is bound to two phenoxide oxygen atoms, with a mean U–O bond length of 2.32(3) Å, an ether oxygen atom, with a larger bond length of 2.583(9) Å, and two bridging hydroxide ions, with a mean bond length of 2.36(1) Å (Table I). These U–O(phenoxide) distances are not significantly larger than those usually observed in calixarene or homooxocalixarene complexes (about 2.28 Å), whereas the U–O(hydroxide) bond length matches that reported in compound **2** [2.36(7) Å]. Ether complexation to uranyl ions has been observed in *p*-methyloctahomotetraoxocalix[4]arene [5], with slightly larger bond lengths [2.661(6) and 2.685(6) Å] and also in *p*-*R*-butylhexahomotrioxocalix[3]arene (*R* = methyl, *tert*-butyl) [16] with an even larger bond length range [2.636(9)–2.950(4) Å]. All these oxygen donors in **1** are equatorial with respect to the uranyl axis. They define a mean plane with a highest deviation of 0.149(6) Å for the ether atom O2, the uranium atom being at 0.026(5) Å from this plane. The uranium atom environment geometry is the usual pentagonal bipyramid. It should be noted that the two aromatic rings corresponding to the uranium-bound phenoxide groups are separated by an oxadimethylene link, and not a methylene one as in compound **2**, and that they are located on the same side of the uranyl mean equatorial plane. As a whole, each homooxocalixarene moiety is bound to two uranyl ions. The remaining phenolic oxygen atoms are not deprotonated and, apart from some of them

TABLE I Selected distances (Å) and angles (°)

Uranium environment						
U–O1	2.295(9)	O1–U–O2	64.2(3)			
U–O2	2.583(9)	O2–U–O3	72.5(3)			
U–O3	2.343(8)	O3–U–O9	78.7(3)			
U–O7	1.774(9)	O9–U–O9'	69.8(4)			
U–O8	1.766(9)	O9'–U–O1	75.4(3)			
U–O9	2.366(8)	O7–U–O8	175.9(4)			
U–O9'	2.347(8)					
Rubidium environment						
Rb1–O3	3.236(10)	Rb2–O4	2.823(10)	Rb3–O5	2.888(11)	
Rb1–O4	3.145(11)	Rb2–O5	3.041(11)	Rb3–O6	3.124(12)	
Rb1–O5	2.950(10)	Rb2–O6''	3.003(10)	Rb3–O7	3.621(12)	
Rb1–O7	2.805(10)	Rb2–O7	3.236(11)	Rb3–O7'''	3.086(12)	
Rb1–O10''	2.98(5)	Rb2–O7'	3.060(10)	Rb3–O10	2.96(5)	
Rb1–O12	3.10(5)			Rb3–O11	2.98(4)	
Rb1–O12'''	2.80(5)					
Rb1–N1	2.871(10)					
Hydrogen bonds						
O4··O3	2.583(13)	O4–H4	1.16	H4··O3	1.60	O4–H4··O3 138
O6··O1'''	2.530(13)	O6–H6	1.10	H6··O1'''	1.54	O6–H6··O1''' 146

Symmetry codes: ' =  $x, 0.5 - y, 1.5 - z$ ; '' =  $1.5 - x, y, 1.5 - z$ ; ''' =  $1.5 - x, 0.5 - y, z$ .

being bound to rubidium ions, they are involved in hydrogen bonds with their phenoxide neighbours (Table I). The two symmetry-related hydroxide ions ensure the dimerization by bridging uranyl ions bound to different macrocycles. The resulting assembly, comprising two homooxalixarenes held by two [(UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub>] groups to give a large anionic capsule, is unprecedented, although it is reminiscent of the *p*-*tert*-butylcalix[6]arene complex of uranyl, in which two macrocycles are bridged by two tetraphenoxide bound uranyl ions [17].

The rubidium ions in **1** are located in the cavity defined by the [(UO<sub>2</sub>)<sub>4</sub>(LH<sub>4</sub>)<sub>2</sub>(OH)<sub>4</sub>]<sup>4-</sup> moiety and, as indicated in the Experimental Section, they are disordered over three positions. These positions, denoted Rb1, Rb2 and Rb3, possess different coordination numbers and geometries. However, because of the important disorder affecting these ions and the water molecules bound to them, some caution in the detailed discussion of this issue is necessary, the presence of some additional water molecules, for example, being possibly masked because of their proximity to rubidium positions. Together with their symmetry equivalents, these three positions define 12 possible sites in the capsule, which may well be occupied somewhat at random. Each of the three positions Rb1, Rb2 and Rb3 is involved in a bond with one or two uranyl oxo groups. Such bonds between alkali metal ions and uranyl oxo groups have been observed in other uranyl coordination compounds [18–21] and were shown to be ubiquitous in the uranyl complexes of *p*-*tert*-butyltetrahomodioxalix[4]arene obtained in the presence of alkali metal hydroxides [9]. The Rb–O(oxo) bond lengths in **1** are in the range 2.805(10)–3.621(12) [mean value 3.2(3)] Å. The smallest distances are similar to the mean values

observed in the previous complexes [9] for K–O(oxo) bonds [mean value 2.8(3) Å], whereas the largest is superior to that observed for Cs–O(oxo) bonds [3.17(8) Å] and therefore may not correspond to a true bond [the mean value if this largest value is disregarded is 3.1(2) Å, intermediate between those for K<sup>+</sup> and Cs<sup>+</sup>, as expected]. As shown in Fig. 3, Rb1 is also bound to the phenoxide oxygen atom O3, which is thus bidentate, the phenol atom O4, the ether atom O5, a pyridine molecule and three water molecules, two of them bridging. Rb2 is bound to the phenolic oxygens O4 and O6, the ether O5 and two oxo groups from different uranyl ions, whereas Rb3 is bound to one phenolic oxygen and one ether oxygen (O6 and O5), two oxo groups and two water molecules. The Rb–O(phenol) bond lengths are in the range 2.823(10)–3.236(10) [mean value 3.1(2)] Å, the Rb–O(ether) in the range 2.888(11)–3.041(11) [mean value 2.96(8)] Å and the Rb–O(water) in the range 2.80(5)–3.10(5) [mean value 3.0(1)] Å. These values agree well with the analogous Rb–O distances reported in the Cambridge Structural Database [22] and with those in the rubidium ion complex of *p*-*tert*-butylthiacalix[4]arene [23]. Note that no obvious cation–π interactions are present in compound **1**, in contrast to what has been observed in previous complexes [6,9].

The ligand LH<sub>4</sub> in compound **1** presents a conformation different from that of L in the tetrauranate complex **2**, as can be seen in Fig. 4. In the latter case, all the oxadimethylene bridges (together with the aromatic carbon atoms to which they are bound) define two *anti* C–O–C–C(arom) torsion angles that give them a “w” shape, as is frequently observed in homooxalixarenes [24]. In the present case, the bridge containing the uranium-coordinated O2 defines one *anti* (161°) and one *gauche* (75°) angle,

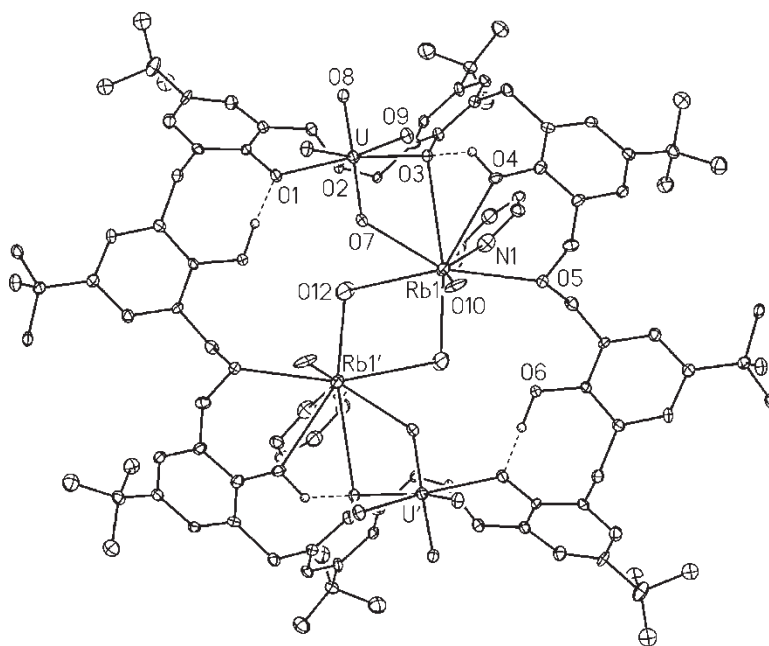


FIGURE 3 View of half the complex molecule in **1**, corresponding to one complete homooxacalixarene. Only one out of the three rubidium positions and its symmetry-related equivalents are represented. Hydrogen atoms omitted for clarity, except for those involved in hydrogen bonds, which are represented as small spheres of arbitrary radii. Hydrogen bonds are represented by dashed lines. Only one position of the disordered *tert*-butyl groups is represented. Ellipsoids are drawn at the 10% probability level. Symmetry code: ' = 1.5 - *x*, 0.5 - *y*, *z*.

which is also a conformation previously encountered [24], but the bridge containing the rubidium-coordinated O5 presents an unprecedented conformation characterized by two *gauche* angles (73 and 80°). These conformations are associated with different coordination geometries: O2 is located

so as to be in the equatorial plane of the uranyl ion, which also contains the two neighbouring phenoxide oxygen atoms, whereas O5 is located so as to be directed towards the centre of the macrocycle cavity, which contains the rubidium ions. The two aromatic rings associated with the uranium-bound atoms O1

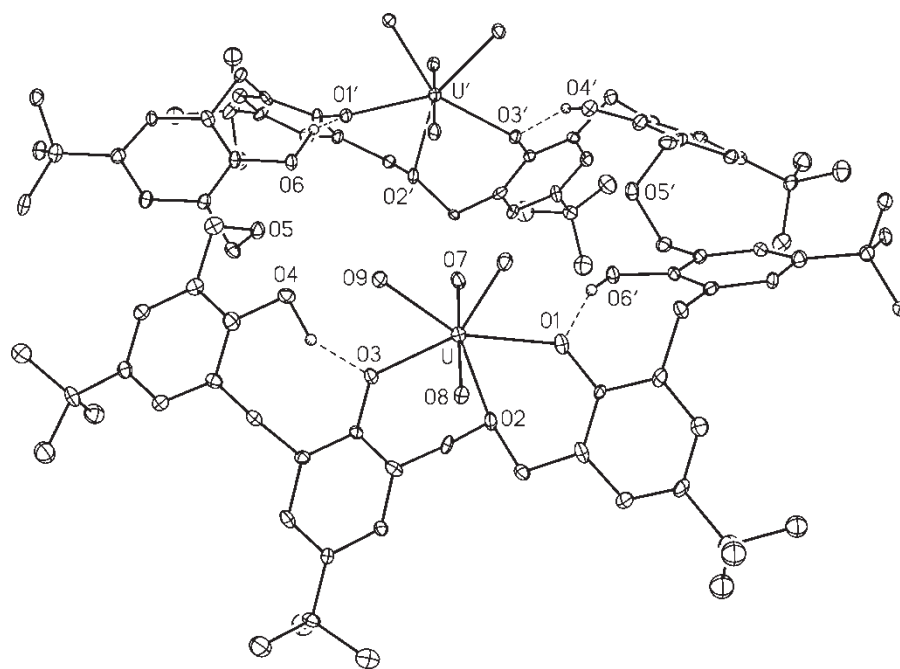


FIGURE 4 View of half the complex molecule in **1**, corresponding to one complete homooxacalixarene, with rubidium ions and water molecules omitted. Hydrogen atoms are omitted for clarity, except for those involved in hydrogen bonds, which are represented by small spheres of arbitrary radii. Hydrogen bonds are represented by dashed lines. Only one position of the disordered *tert*-butyl groups is represented. Ellipsoids are drawn at the 10% probability level. Symmetry code: ' = 1.5 - *x*, 0.5 - *y*, *z*.

and O3 define a dihedral angle of  $56^\circ$ , its concave side being directed away from the inside of the macrocycle. Successive phenolic groups linked by hydrogen bonds are those separated by methylene bridges, the latter defining  $g^+g^-$  torsion angle sequences, that is each of these diphenolic units assumes the conformation of half a *p-tert*-butylcalix[4]arene in the *cone* conformation. The macrocycle conformation is in general very irregular because of the presence of the highly flexible oxadimethylene links and the requirements of the complexed cations.

In the presence of lithium hydroxide, no crystal of satisfactory quality was obtained, but a rough structural model could be determined (see Experimental Section). Despite the numerous uncertainties, even with regard to the  $\text{UO}_2/\text{Li}$  stoichiometry and deprotonation of the ligand, it can be stated that the macrocycle acts as a ditopic ligand with two tetraphenolic sites approximately perpendicular to each other and separated by a pinched region formed by two ether bridges. Each of these sites encompasses a uranyl ion bound in an "internal" manner by all four oxygen atoms, whereas the lithium ions seem to be located outside, with at least one of them involved in a bond with a uranyl oxo group (as in the case of *p-tert*-butyltetrahomodioxacalix[4]arene [9]). The many differences between these two structures, with  $\text{Rb}^+$  and  $\text{Li}^+$ , indicate that any prediction of the behaviour of such a large and flexible macrocycle must be subject to caution, in contrast to the situation with smaller homooxacalixarenes [9].

The present complex can be described as a dimeric calixarene assembly held by two  $[(\text{UO}_2)_2(\text{OH})_2]$  moieties and defining an inner cavity containing a cluster of four rubidium ions and at least four water molecules, all very disordered. As in previous molecular boxes built around uranyl ions [25,26], the oxo group directed inwards serves as a binding site for the host molecule/ion. Such a combination of a well-defined envelope and a disordered inner assembly has been described in some alkali metal ion complexes of *p-tert*-butylthiacalix[4]arene [23], but in this case, only one species of metal ions is present and acts as links between different calixarenes. Apart from the unprecedented macrocycle/uranyl hydroxide dimer structure, the originality of the present case is the coexistence of two very different metal ions, resulting in a large octanuclear assembly with

a geometry seemingly defined primarily by the uranyl cation, which has the more rigid coordination geometry requirements and is a powerful assembling moiety [25–27].

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