

Oxa- and Azacalixarenes as Ligands for Uranyl Ions – Evidence for Two Different Complexation Modes

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Keywords: Uranium / Calixarenes / Zwitterion / Crystal structure

The first crystal structures are reported for uncomplexed parent tetrahomodioxo- and tetrahomodiazacalix[4]arene compounds and their 1:1 uranyl complexes. A 1:1 uranyl complex is also reported for a hexahomotriazacalix[3]arene. While analogous features are observed for the uncomplexed dioxo- and diazacalixarenes, completely different coordination modes are observed in their uranyl complexes. The complex of *p*-*tert*-butyltetrahomodioxacalix[4]arene is obtained in the presence of triethylamine and consists of an anionic core in which the cation is located at the centre of the lower rim, as is frequently observed. Both *p*-chloro-*N*-benzyl-hexahomo-

triazacalix[3]arene and *p*-methyl-*N*-benzyl-tetrahomodiazacalix[4]arene react with uranyl nitrate without adding a basic agent. The resulting 1:1 complexes are neutral, the cation being located outside the macrocycle and bound to two phenoxide groups of its zwitterionic form and to the nitrate counter-ions. The difference in coordination mode between homooxa- and homoazacalixarene complexes is attributed to the electrostatic repulsion between the uranyl ions and the ammonium groups located around the lower rim in the latter case, which prevents a close approach of the complexed cation.

Introduction

The work of Shinkai et al., who demonstrated about ten years ago the “uranophile” potential of water-soluble calixarenes, generated an interest that led to the investigation of uranyl complexes of calixarenes.^[1] Unfortunately, the crystal structures of the complexes involved have never been elucidated due to the difficulties encountered in growing single crystals. However, since then a lot of structural information has been gathered about the uranyl complexes of parent calix[*n*]arenes (*n* between 5 and 9 and *n* = 12) and homooxacalixarenes,^[2] whereas only one crystal structure involving coordinating pendent arms grafted on a calix[4]arene has been reported.^[3] Parent calixarenes and homooxacalixarenes readily form uranyl complexes in a basic medium. These are either mononuclear with the smallest calixarenes in cone conformation (*p*-*tert*-butyldihomo-

oxacalix[4]arene,^[2a] *p*-*tert*-butylhexahomotrioxacalix[3]arene,^[2i] *p*-*tert*-butylcalix[5]arene^[2e]) or polynuclear with larger, flattened calixarenes (*p*-*tert*-butylcalix[8]arene,^[2b,2c,2k] *p*-*tert*-butylcalix[9]arene,^[2k] *p*-*tert*-butylcalix[12]arene^[2j]). *p*-*tert*-Butylcalix[6]arene gives only external complexes with a 2:1,^[2g] 2:2^[2d] or 3:3^[2k] metal:ligand stoichiometry. Calix[7]arene is another peculiar case, being able to engage in complexation only one of its two (trimeric and tetrameric) subunits,^[2f] or both.^[2h] The complex formed by *p*-*tert*-butylhexahomotrioxacalix[3]arene (ligand **1** in Scheme 1) is of particular interest since it constitutes the first and, up to now, the only example of a pseudo-trigonal equatorial coordination for the uranyl ion.^[2i]

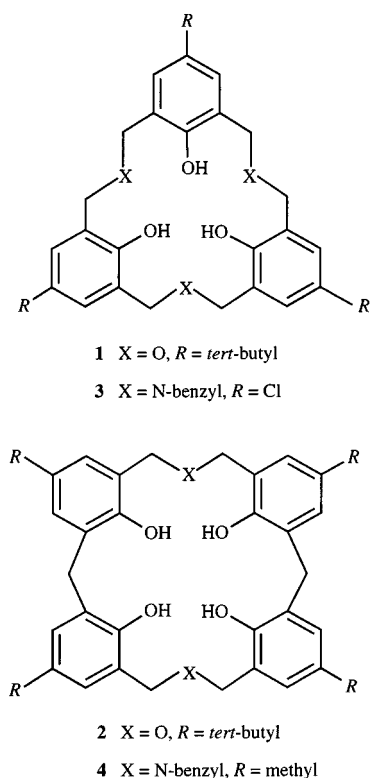
The homooxa- and homoazacalixarenes are less rigid than calixarenes, as shown by ¹H NMR spectroscopic measurements in the case of the former.^[4] Furthermore, they possess two different kinds of potential binding sites, and homoazacalixarenes, which were first synthesized some years ago,^[5] can bear various substituents on the amine nitrogen atom. The metal-ion complexes of homooxacalixarenes thus far reported have been obtained classically in a basic medium.^[2a,2i,6] In order to further investigate the complexing properties of these ligands, we synthesized, in the presence of triethylamine, the uranyl complex of another oxacalixarene, *p*-*tert*-butyltetrahomodioxacalix[4]arene (**2**), the structure of which is reported herein as well as that of the uncomplexed ligand. We have recently begun the investigation of azacalixarenes as ligands and reported the crystal structures of *p*-chloro-*N*-benzylhexahomotriazacalix[3]arene (**3**) and of its mononuclear complex with neodymium nitrate.^[7] This work demonstrated a peculiarity of the homoazacalixarenes as ligands in that they are able to com-

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Scheme 1. The homooxa- and homoazacalixarenes under study

plex lanthanide ions without the addition of a basic agent such as the commonly used triethylamine or 1,4-diazabicyclo[2.2.2]octane (DABCO), owing to the displacement of the protons from oxygen to nitrogen atoms (zwitterionic or amphiionic form) upon complexation. We report herein the synthesis in a neutral medium as well as the crystal structures of the uranyl complexes of two azacalixarenes, **3** and *p*-methyl-*N*-benzyltetrahomodiazacalix[4]arene (**4**), and the crystal structure of the uncomplexed molecule **4**. Unfortunately, we have not succeeded in growing single crystals of the complex species obtained with **3** and **4** in a basic medium, for comparative purposes. To the best of our knowledge, the crystal structures reported herein are the first ones for parent tetrahomodioxo- and tetrahomodiazacalix[4]arenes and their complexes.

Results and Discussion

Uncomplexed Calixarenes

The asymmetric unit in **2**·2CH₃CN (**5**) is composed of half a molecule, located around a binary axis perpendicular to its mean plane (Figure 1). The overall shape is that of a very distorted cone, and is determined by an intramolecular hydrogen bonding array which links both phenolic and ether groups (Table 1). The two ether links, which give the molecule its high flexibility, are positioned so as to bring the ether atom O(2) and its symmetry-related equivalent O(2') close to the protons of the phenolic atoms O(3) and O(3'). However, the macrocycle is not large enough to prevent the formation of a cyclic hydrogen bonding array link-

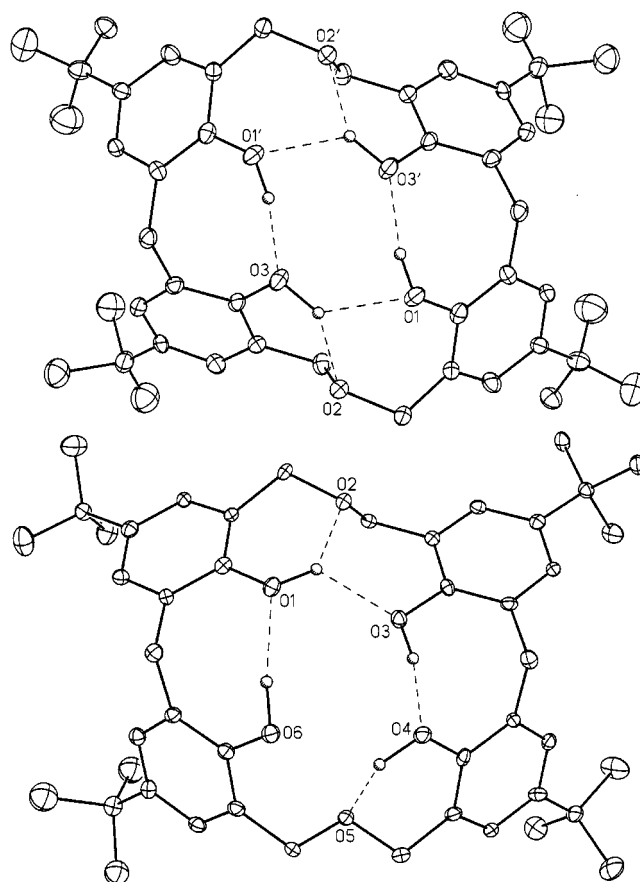


Figure 1. View of *p*-*tert*-butyltetrahomodioxacalix[4]arene **5** (top) and in **6** (bottom), showing the difference in hydrogen bonding patterns; hydrogen bonds in dashed lines; hydroxyl protons represented as small spheres of arbitrary radii; other hydrogen atoms and solvent molecules omitted for clarity; symmetry code: ' = y, x, -z

ing the four phenolic oxygen atoms, with O(3) and O(3') giving a bifurcated hydrogen bond, the O(3)···O(2) bond being stronger than O(3)···O(1). The calixarene shape can be characterized by the values of the dihedral angles between the phenolic rings and the mean plane defined [$\pm 0.339(4)$ Å] by the phenolic oxygen atoms, which are 38.8(2) and 47.2(2)° [mean value 43(6)°]. The cup shape is sufficiently deep for the two acetonitrile molecules (not involved in hydrogen bonding) to be included in the cavity: such a situation has already been observed in the case of *p*-*tert*-butylcalix[6]arene,^[8] which confirms the similarity between the two ligands in terms of cavity size.^[9]

The asymmetric unit in **2**·2.5C₃H₅N (**6**) is composed of one molecule, represented in Figure 1, the overall features of which are analogous to those in **5**. However, the calixarene conformation is different in the surroundings of atom O(5), which results in a slight enlargement of the macrocycle and the breaking of one of the hydrogen bonds. The interest of this structure is to show that, depending upon the solvent, it is possible to observe conformations of the ether bridge which do not allow bifurcate hydrogen bonds. The values of the dihedral angles between the phenolic rings and the mean plane defined [$\pm 0.188(2)$ Å] by the phenolic

Table 1. Selected bond lengths (Å) and angles (°)

Uranium environment							
8							
U–O(1)	2.272(4)	U–O(6)	2.333(4)	O(1)–U–O(3)	94.4(2)	O(6)–U–O(1)	84.8(2)
U–O(3)	2.252(4)	U–O(7)	1.795(4)	O(3)–U–O(4)	87.5(2)	O(7)–U–O(8)	178.3(2)
U–O(4)	2.269(4)	U–O(8)	1.804(4)	O(4)–U–O(6)	93.3(2)		
9							
U–O(1)	2.284(7)	U–O(5)	1.772(7)	U–O(9)	2.578(7)	O(6)–U–O(7)	49.2(2)
U–O(3)	2.278(7)	U–O(6)	2.576(7)	U–O(10)	2.586(7)	O(9)–U–O(10)	49.3(2)
U–O(4)	1.771(8)	U–O(7)	2.586(9)	O(1)–U–O(3)	75.1(3)	O(4)–U–O(5)	175.0(3)
10							
U–O(1)	2.234(9)	U–O(6)	1.758(9)	U–O(10)	2.398(10)	O(5)–U–O(6)	176.4(4)
U–O(2)	2.269(8)	U–O(7)	2.530(9)	O(1)–U–O(2)	78.9(3)		
U–O(5)	1.757(8)	U–O(8)	2.504(10)	O(7)–U–O(8)	50.3(4)		
Hydrogen bonds ^[a]							
5							
O(1)···O(3')	2.787(7)	O(1)–H	0.94	H···O(3')	1.91	O(1)–H···O(3')	155
O(3)···O(1)	2.915(7)	O(3)–H	1.09	H···O(1)	2.08	O(3)–H···O(1)	131
O(3)···O(2)	2.753(7)			H···O(2)	1.89	O(3)–H···O(2)	133
6							
O(1)···O(2)	2.743(5)	O(1)–H	1.11	H···O(2)	1.81	O(1)–H···O(2)	139
O(1)···O(3)	2.989(5)			H···O(3)	2.16	O(1)–H···O(3)	129
O(3)···O(4)	2.763(5)	O(3)–H	1.05	H···O(4)	1.74	O(3)–H···O(4)	166
O(4)···O(5)	2.657(5)	O(4)–H	1.09	H···O(5)	1.79	O(4)–H···O(5)	133
O(6)···O(1)	3.147(5)	O(6)–H	1.09	H···O(1)	2.23	O(6)–H···O(1)	140
7							
O(1)···O(4)	2.861(4)	O(1)–H	0.88	H···O(4)	1.99	O(1)–H···O(4)	177
O(2)···O(1)	2.903(3)	O(2)–H	1.08	H···O(1)	2.49	O(2)–H···O(1)	102
O(2)···N(1)	2.692(4)			H···N(1)	1.64	O(2)–H···N(1)	165
O(3)···O(2)	2.820(3)	O(3)–H	0.94	H···O(2)	1.89	O(3)–H···O(2)	173
O(4)···O(3)	2.946(3)	O(4)–H	1.05	H···O(3)	2.48	O(4)–H···O(3)	106
O(4)···N(2)	2.713(4)			H···N(2)	1.85	O(4)–H···N(2)	137
8							
N(1)···O(8)	2.728(7)	N(1)–H	0.99	H···O(8)	1.77	N(1)–H···O(8)	163
N(2)···O(6)	2.715(7)	N(2)–H	1.05	H···O(6)	1.72	N(2)–H···O(6)	157
9							
N(1)···O(1)	2.95(1)	N(1)–H	0.92	H···O(1)	2.44	N(1)–H···O(1)	116
N(1)···O(2)	2.64(1)			H···O(2)	1.91	N(1)–H···O(2)	136
N(2)···O(2)	2.61(1)	N(2)–H	1.11	H···O(2)	1.74	N(2)–H···O(2)	132
N(2)···O(3)	2.97(1)			H···O(3)	2.20	N(2)–H···O(3)	124
N(3)···O(1)	2.91(1)	N(3)–H	1.05	H···O(1)	2.37	N(3)–H···O(1)	111
N(3)···O(3)	2.84(1)			H···O(3)	1.92	N(3)–H···O(3)	145
10							
N(1)···O(1)	2.88(1)	N(1)–H	0.99	H···O(1)	2.21	N(1)–H···O(1)	124
N(1)···O(2)	2.86(1)			H···O(2)	2.14	N(1)–H···O(2)	128
N(2)···O(3)	2.78(1)	N(2)–H	0.97	H···O(3)	2.07	N(2)–H···O(3)	128
N(2)···O(4)	2.79(1)			H···O(4)	1.97	N(2)–H···O(4)	141
O(3)···O(2)	2.62(1)	O(3)–H	1.09	H···O(2)	1.66	O(3)–H···O(2)	145
O(4)···O(1)	2.69(1)	O(4)–H	1.03	H···O(1)	1.81	O(4)–H···O(1)	145

^[a] Symmetry code: ' = *y*, *x*, *−z*.

oxygen atoms are 38.5(2), 22.7(2), 46.8 (2) and 70.6(1)°, which indicate a strong deviance with respect to a regular cone shape. Two pyridine molecules, roughly orthogonal to each other and not involved in hydrogen bonding, are located in the calixarene cavity.

The asymmetric unit in **4**·CH₃CN (**7**) comprises one molecule, without any crystallographic symmetry (Figure 2). The conformation of the calixarene is strikingly similar to that observed in **5**, with a similar hydrogen bonding pattern. The hydrogen bonds linking the phenolic oxygen atoms between them [O(1)···O(2) and O(3)···O(4)] are however much weaker than their counterparts in **5**: such a predominance of OH···N bonds over OH···O ones has already been encountered in **3**, but was less pronounced.^[7] The values of the dihedral angles between the four phenolic rings and the

mean plane defined [$\pm 0.321(1)$ Å] by the phenolic oxygen atoms are 41.1(1), 43.0(1), 30.0(1) and 41.1(1)°, [mean value 39(6)°] comparable to those in **5**. However, in the present case, the cavity, which is not as deep as in **5** and **6**, due to the replacement of *tert*-butyl by methyl substituents, is empty. The benzyl substituents are directed towards the exterior of the macrocycle, on the lower rim side.

If the uncomplexed oxa- and azacalixarenes present closely related features, the basic nature of the nitrogen atoms in the latter results in different complexing behaviours, exemplified hereafter in the case of uranyl ions.

Uranyl Ion Complexes

The complexation of one uranyl ion by **2** in the presence of NEt₃ to give [UO₂(**2** – 4H)]^{2−}(HNEt₃⁺)₂·CHCl₃·

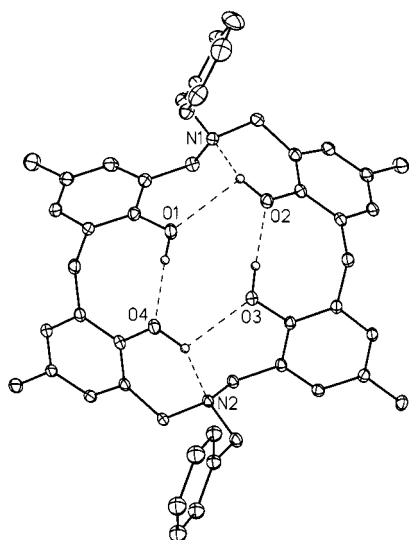


Figure 2. View of *p*-methyl-*N*-benzyltetrahomodiazacalix[4]arene **4** in **7**; hydrogen bonds in dashed lines; hydroxyl protons represented as small spheres of arbitrary radii; other hydrogen atoms and solvent molecule omitted for clarity; only the main component of disordered atoms is represented

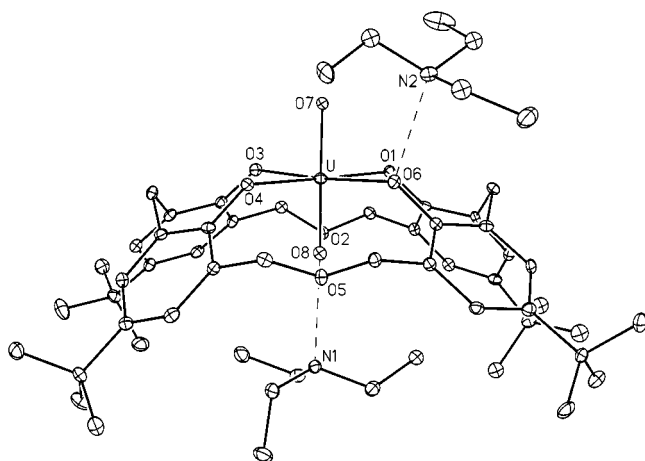


Figure 3. View of the "internal" uranyl ion complex of *p*-*tert*-butyltetrahomodioxacalix[4]arene **8**; hydrogen bonds in dashed lines; hydrogen atoms and solvent molecules omitted for clarity; only the main component of disordered atoms is represented

CH₃CN (**8**) is accompanied by a conformational change of the macrocycle. As illustrated in Figure 3, the cation is located at the centre of the lower rim, with its main axis perpendicular to it, and bound to the four deprotonated oxygen atoms [mean U–O distance 2.28(3) Å, as observed previously for phenoxide groups^[2]]. The molecule presents two orthogonal non-crystallographic symmetry planes with the uranyl axis at their intersection and passing through either the methylene or the ether bridges. Such a square planar equatorial geometry is rather common in calixarene complexes, having been observed in the complexes of *p*-*tert*-butyldihomooxacalix[4]arene,^[2a] *p*-*tert*-butylcalix[7]arene^[2f] and *p*-benzylcalix[7]arene,^[2h] but it is rarely so regular [mean O_{phenol}–U–O_{phenol} angle between adjacent phenolic units 90(5)°, mean O_{uranyl}–U–O_{phenol} angle 90(2)°]. In particular, with respect to *p*-*tert*-butyldihomooxacalix[4]arene,

the presence of a second ether link in **2** permits a more symmetrical geometry around the cation. The ether oxygen atoms were not coordinated in the two other uranyl complexes of oxacalixarenes reported.^[2a,2i] Also, in the present case, the two ether oxygen atoms are clearly non bonding, being at distances of 3.832(4) and 3.820(4) Å from the uranium atom [values larger than in the previous cases: 3.534(8)^[2a] and 3.1(1)^[2i] Å] and at distances of 1.812(6) and 1.893(6) Å from the mean plane defined [$\pm 0.027(2)$ Å] by the four coordinating oxygen atoms. The disruption of the hydrogen bonding pattern of **2** and the location of the four phenolic oxygen atoms in a plane result in a conformation different from those observed in **5** and **6**. The values of the dihedral angles between the four phenolic rings and the mean plane defined by the phenolic oxygen atoms are 47.9(2), 40.0(1), 48.3(1) and 42.9(2)° [mean value 45(4)°]. The two triethylammonium counter-ions in **8** are located as frequently observed, one of them hydrogen bonded to an uranyl oxo atom and included in the calixarene cavity and the other hydrogen bonded to a phenoxide group. We have mentioned above the similarity in size between *p*-*tert*-butyltetrahomodioxacalix[4]arene and *p*-*tert*-butylcalix[6]arene; however, these ligands appear very different from equivalent towards uranyl complexation, since the latter gives "external" complexes only.^[2d,2g,2k]

Whereas the uranyl ion is located at the centre of the lower rim in the three complexes of oxacalixarenes presently reported, the coordination mode in the complex of the azacalixarene **3**, obtained without a basic agent being added, is completely different. The asymmetric unit in [UO₂(NO₃)₂·3]·C₅H₅N·CHCl₃ (**9**) comprises one molecule (Figure 4), which does not possess any true symmetry element, but presents a pseudo symmetry plane containing the atom O(2) and the uranyl ion. The cation is located outside the lower rim array and is bound to two phenoxide ions

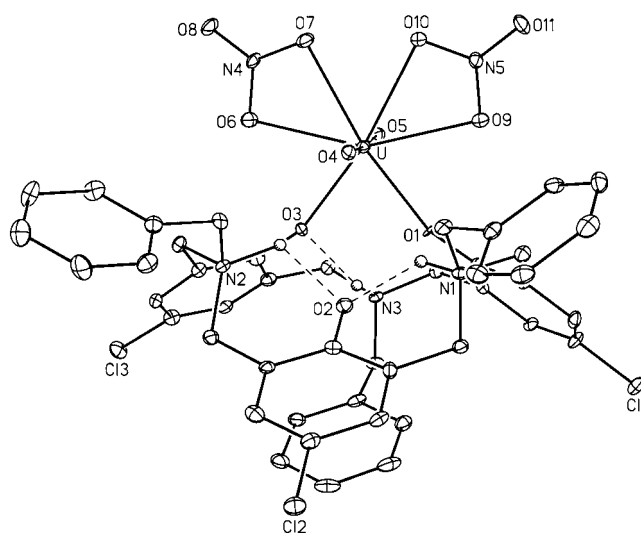


Figure 4. View of the "external" uranyl ion complex of *p*-chloro-*N*-benzylhexahomotriazacalix[3]arene **9**; hydrogen bonds in dashed lines; protons of the ammonium groups represented as small spheres of arbitrary radii; other hydrogen atoms and solvent molecules omitted for clarity

only, with its axis roughly parallel to the mean plane of the molecule. The coordination sphere is completed by two bidentate nitrate ions. Such a six-coordinate environment is unusual in uranyl complexes of calixarenes and is due to the small-bite nature of nitrate ions. The uranium atom is located at 1.556(7) Å from the mean plane defined by the three phenoxide oxygen atoms, a value comparable to that of the neodymium(III) complex of **3** [1.591(2) Å]^[7] which presents many similarities with **9** (an obvious difference being that the neodymium ion is bound to the three phenoxide oxygen atoms). In both complexes, the three phenolic protons have been transferred to the amine groups upon complexation. An asymmetric array of hydrogen bonds links the ammonium and phenoxide groups in **9**, as in the Nd³⁺ complex. The values of the three dihedral angles between the phenolic rings and the mean plane defined by the three phenolic oxygen atoms are 64.6(3), 2.23(9) and 60.2(3)°; those values are different from those in both the uncomplexed molecule **3** and its Nd³⁺ complex. In the latter case, one of the rings was nearly parallel to the mean plane, as the one corresponding to the non-coordinated phenolic group in **9**, but the two other rings are much more “vertical” in **9**. Two benzyl substituents are located on the lower rim side and directed towards the exterior of the macrocycle whereas the third one is on the upper rim side and directed towards the cavity, in which it occupies a position nearly parallel to that of the uncomplexed phenolic ring.

The question arises as to the role of the acid-enhancing *p*-chlorine substituent in the auto-deprotonation process leading to complex **9** as well as to the Nd³⁺ complex of **3**. Complex **10** brings an answer as well as an interesting point of comparison with complex **8**. The complexation by ligand **4** occurs also without a basic agent being added, giving [UO₂(NO₃)₂·**4**]·0.5CH₃OH·H₂O (**10**) in which the complex molecule is neutral. This reaction indicates that the pres-

ence of chlorine atoms is not necessary to promote the protons transfer. The asymmetric unit in **10** comprises one complex molecule lacking any symmetry element (Figure 5). The uranyl ion is bound to two phenoxide groups, as in **9**, and its distance from the mean plane defined [$\pm 0.030(5)$ Å] by the four calixarene oxygen atoms is 1.543(8) Å. The two nitrate counter-ions behave differently: one is bidentate and the other monodentate. This difference with **9** may be ascribed to an O_{phenol}–U–O_{phenol} angle slightly larger in **10** [78.9(3)° to be compared with 75.1(3)° in **9**], which could make the available space insufficient for two bidentate nitrate ions. The two coordinated phenolic groups are deprotonated and the two amine groups are turned into ammonium cations. Hydrogen bonds are formed between each ammonium group and its two neighbouring oxygen atoms, and also between the two non-coordinated, protonated, oxygen atoms O(3) and O(4) and the two phenoxide groups. The modification of the hydrogen bonding pattern with respect to **7** results in a different calixarene conformation. The values of the dihedral angles between the four phenolic rings and the mean oxygen atoms plane are 61.7(3), 59.1(3), 21.0(4) and 16.1(5)°, the two uncomplexed phenolic moieties being closer to the mean plane. Two half-cones are defined on each side of the N(1)⋯N(2) axis, but their junction does not give an overall cone conformation: the usual terms defining the conformation of classical small calixarenes are of no practical use in the present case, which is reminiscent of larger, flattened calixarenes.

The question arises of the origins of the difference in coordination mode between the uranyl complex of *p*-tert-butylhexahomotrioxacalix[3]arene and **8** on the one hand and **9** and **10** on the other. The main reason is likely to be the electrostatic repulsion between the uranyl cation and the two or three ammonium groups in the latter cases, which prevents the cation from being located in the mean plane

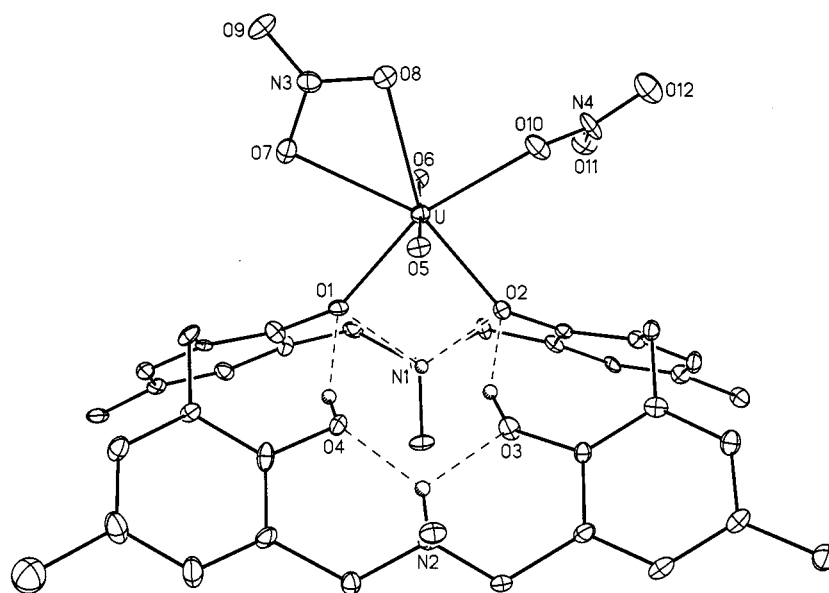


Figure 5. View of the “external” uranyl ion complex of *p*-methyl-*N*-benzyltetrahomodiazacalix[4]arene **10**; hydrogen bonds in dashed lines; protons of the hydroxyl and ammonium groups represented as small spheres of arbitrary radii; other hydrogen atoms, benzyl groups and solvent molecules omitted for clarity

defined by the lower rim. An influence of the steric hindrance associated with the benzyl groups occupying the cavity is not likely, due to the high flexibility of these substituents and the high affinity of phenoxide groups for uranyl ions. In spite of repeated attempts, we did not succeed in growing single crystals of the complex species obtained with azacalixarenes in a basic medium (NEt_3 or DABCO), for comparative purposes. It may be assumed that the deprotonation of the ligand by the base could lead to an anionic complex with a coordination mode closer to that observed with other calixarenes. It must be noted that, by contrast with all the uranyl complexes of calixarenes reported up to now, the azacalixarene complexes **9** and **10** are neutral and not anionic, since the ligand itself is neutral and the metal cation is bound to its counter-ions.

The interest of zwitterions for the simultaneous solvent extraction of cations and anions has recently been pointed out and exemplified by a Schiff base bearing morpholine groups.^[10] In this case, the Schiff base with deprotonated hydroxyl groups complexes the metal ion while the protonated morpholine groups complex the counter-ion. The situation is somewhat different in the case of azacalixarenes since the cationic part of the ligand is not directly involved in complexation, but simply pushes the cation into an "external" position in which it cannot reach its usual coordination number from the calixarene and must remain bound to its counter-ions.

Experimental Section

Synthesis

***p*-tert-Butyltetrahomodioxacalix[4]arene (2):** This compound was synthesized as previously reported.^[11] Slow evaporation of a solution of **2** in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (1:1) gave colourless single crystals of **2**· $2\text{CH}_3\text{CN}$ (**5**) suitable for X-ray crystallography, whereas slow evaporation of a solution in pyridine gave colourless single crystals of **2**· $2.5\text{C}_5\text{H}_5\text{N}$ (**6**) of lower quality.

***p*-Methyl-*N*-benzyl-tetrahomodiazacalix[4]arene (4):** A solution of *p*,*p'*-methylenebis(4-methyl-6-hydroxymethyl)phenol (8.00 g, 27.8 mmol) and benzylamine (3.4 g, 31.7 mmol) in 100 mL of xylene was heated under reflux for 34 h. After removal of the solvent under reduced pressure, the resultant oily material was subjected to silica-gel column chromatography with CH_2Cl_2 as an eluent. **4** was obtained as a colourless powder (5.81 g, yield 58.3%). The analytical sample was recrystallized from $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$. M.p. 146–148 °C. — ^1H NMR (270 MHz, CDCl_3): δ = 2.17 (s, 12 H, Ar-CH₃), 3.43, 3.60, 4.25 (3bs, 16 H, Ar-CH₂-), 6.69 (d, J = 2 Hz, 4 H, Ar-H), 7.03 (d, J = 2 Hz, 4 H, Ar-H), 7.34 (br. s, 10 H, side arm Ar-H), 10.6 (br. s, 4 H, Ar-OH). — $\text{C}_{48}\text{H}_{50}\text{N}_2\text{O}_4 \cdot 0.5\text{C}_2\text{H}_5\text{OH}$ (741.93): calcd. C 79.32, H 7.20, N 3.78; found C 79.11, H 7.35, N 3.67. Concentration of the mother liquor also afforded 0.31 g (3.3%) of *p*-methyl-*N*-benzyl-dihomoazacalix[4]arene. Slow evaporation of a solution of **4** in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (1:1) gave colourless single crystals of **4**· CH_3CN (**7**) suitable for X-ray crystallography.

$[\text{UO}_2(2 - 4\text{H})]^{2-}(\text{HNEt}_3^+)_2 \cdot \text{CHCl}_3 \cdot \text{CH}_3\text{CN}$ (8**):** Compound **2** (0.02 g, 0.03 mmol) was dissolved in 6 mL of $\text{CH}_3\text{CN}/\text{CHCl}_3$ (1:1)

and 1 mL of NEt_3 ; a solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.03 g, 0.06 mmol) in 2 mL of CH_3CN was then added dropwise, immediately giving an orange solution, which was allowed to slowly evaporate. A few orange single-crystals suitable for X-ray crystallography deposited in three days together with a microcrystalline powder. Microanalysis results including both crystals and powder were unsatisfactory due to the heterogeneous nature of the latter.

$[\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{C}_5\text{H}_5\text{N} \cdot \text{CHCl}_3$ (9**):** Compound **3** (0.15 g, 0.19 mmol) was dissolved in 30 mL of $\text{CH}_3\text{CN}/\text{CHCl}_3$ (1:1) and a solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3 g, 0.6 mmol) in 30 mL of CH_3CN was added dropwise, immediately giving an orange solution. Orange single crystals, unstable out of their mother solution but suitable for X-ray crystallography, were obtained upon recrystallization from pyridine. — $[\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{C}_5\text{H}_5\text{N} \cdot \text{CHCl}_3 \cdot \text{H}_2\text{O}]$, $\text{UC}_{46}\text{H}_{45}\text{Cl}_6\text{N}_5\text{O}_{12}$ (1310.60): calcd. C 42.16, H 3.46; found C 42.06, H 3.35. — FAB-MS $[\text{UO}_2 \cdot \text{C}_{45}\text{H}_{42}\text{Cl}_3\text{N}_3\text{O}_3]$: m/z = calcd. 1047.26; found 1048.2.

$[\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{C}_5\text{H}_5\text{N} \cdot 0.5\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (10**):** Compound **4** (0.04 g, 0.055 mmol) was dissolved in 3 mL of CHCl_3 and a solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.04 g, 0.08 mmol) in 5 mL of CH_3OH was added dropwise, immediately giving an orange solution. Orange single crystals suitable for X-ray crystallography were obtained in a few hours. — $\text{UC}_{48.5}\text{H}_{54}\text{N}_4\text{O}_{13.5}$ (1146.99): calcd. C 50.79, H 4.75; found C 50.28, H 4.28.

Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer^[12] using graphite-monochromated Mo- K_α radiation (0.71073 Å). The crystals were introduced in Lindemann glass capillaries with a protecting "Paratone" oil (Exxon Chemical Ltd.) coating. The data were processed with DENZO-SMN.^[13] The structures were solved by direct methods with SHELXS-97^[14] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.^[15] No absorption correction was done for **5**, **6** and **7**, the product $\mu \cdot d$ being lower than 0.1. Absorption effects in **8**, **9** and **10** were corrected empirically with the program MULABS from PLATON.^[16] Hydroxyl and ammonium protons, as well as those of chloroform molecules, were introduced as found on the Fourier difference maps whereas all other hydrogen atoms in all compounds were introduced at calculated positions (except in the disordered parts). All hydrogen atoms were treated as riding atoms with a displacement parameter equal to 1.2 (OH, NH, CH, CH₂) or 1.5 (CH₃) times that of the parent atom. All non-hydrogen atoms were refined anisotropically, except the disordered ones. Special features for each compound are indicated in the following.

2· $2\text{CH}_3\text{CN}$ (5**):** The data were recorded at ambient temperature since the crystals deteriorate at low temperature, which is seemingly due to a phase transition phenomenon. Some soft restraints have been applied on the badly resolved acetonitrile molecules. The absolute structure could not be determined from the value of the Flack parameter.^[17]

2· $2.5\text{C}_5\text{H}_5\text{N}$ (6**):** One *tert*-butyl substituent was found disordered over two positions, which have been refined with occupation factors constrained to sum to unity. The nitrogen atoms were not located in the pyridine molecules (one of them disordered around a symmetry centre).

4· CH_3CN (7**):** One of the two benzyl substituents was disordered over two positions sharing two carbon atoms, which have been refined with occupation factors constrained to sum to unity.

$[\text{UO}_2(2 - 4\text{H})]^{2-}(\text{HNEt}_3^+)_2 \cdot \text{CHCl}_3 \cdot \text{CH}_3\text{CN}$ (8**):** Some disorder was present on one *tert*-butyl group and one triethylammonium

Table 2. Crystal data and structure refinement details

	5	6	7	8	9	10
Empirical formula	C ₅₀ H ₆₆ N ₂ O ₆	C _{58.5} H _{72.5} N _{2.5} O ₆	C ₅₀ H ₅₃ N ₃ O ₄	UC ₆₁ H ₉₂ Cl ₃ N ₃ O ₈	UC ₅₁ H ₄₈ Cl ₆ N ₆ O ₁₁	UC _{48.5} H ₅₄ N ₄ O _{13.5}
<i>M</i> /g mol ^{−1}	791.02	906.69	759.95	1339.76	1371.68	1146.99
<i>T</i> /K	293(2)	120(2)	293(2)	100(2)	100(2)	100(2)
Crystal system	Tetragonal	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Tetragonal
Space group	<i>P</i> 4 ₁ 2 ₁ 2	<i>C</i> 2/ <i>c</i>	<i>P</i> 1	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> <i>c</i>	<i>P</i> 4 ₃ 2 ₁ 2
<i>a</i> /Å	17.329(2)	34.380(4)	10.943(2)	12.4313(3)	9.3345(5)	13.882(1)
<i>b</i> /Å	17.329(2)	9.2515(5)	13.132(2)	16.7223(4)	25.283(2)	13.882(1)
<i>c</i> /Å	15.594(2)	36.161(4)	16.485(2)	30.4446(8)	22.924(1)	48.292(5)
<i>a</i> / °	90	90	79.026(10)	90	90	90
<i>β</i> / °	90	116.936(3)	74.077(9)	90	94.634(4)	90
<i>γ</i> / °	90	90	72.397(7)	90	90	90
<i>V</i> /Å ³	4683(1)	10254(2)	2156.4(6)	6328.8(3)	5392.5(5)	9306(2)
<i>Z</i>	4	8	2	4	4	8
<i>μ</i> /mm ^{−1}	0.072	0.075	0.074	2.744	3.372	3.560
Reflections collected	27912	34044	15878	43757	18296	20655
Independent reflections	4010	9194	7319	11953	9392	6748
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	1230	4252	3940	10505	8301	4812
<i>R</i> _{int}	0.124	0.184	0.064	0.088	0.068	0.121
<i>R</i> ₁	0.083	0.101	0.080	0.042	0.050	0.060
<i>wR</i> ₂	0.169	0.206	0.201	0.090	0.122	0.111

ion, which was modelled with two positions refined with occupation factors constrained to sum to unity. The absolute structure was determined from the value of the Flack parameter [−0.015(6)].

[UO₂(NO₃)₂·3]·C₅H₅N·CHCl₃ (9): The absolute structure was determined from the value of the Flack parameter [−0.013(7)].

[UO₂(NO₃)₂·4]·0.5CH₃OH·H₂O (10): The two benzyl substituents were found disordered over two positions each. These four positions, which have been refined with occupation factors constrained to sum to unity for each benzyl moiety, overlap between neighbouring molecules and share one or two atomic positions. The occupation parameters have been chosen so as to take into account the impossibility of a simultaneous occupation of overlapping positions. The methanol solvent molecule was also found disordered over two sites symmetrically related, each affected with a 0.5 occupation. The structure was refined as corresponding to a racemic twin, the fractional contribution of the two components being *x* and (1 − *x*), with *x* = 0.504(14).

Crystal data and structure refinement parameters are given in Table 2. The molecular plots were drawn with SHELXTL.^[18] All calculations were performed on a Silicon Graphics R5000 workstation.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144187–144192 (5–10). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Received May 22, 2000

[I00212]