Supramolecular assemblies from uranyl ion complexes of hexahomotrioxacalix[3]arenes and protonated [2.2.2]cryptand

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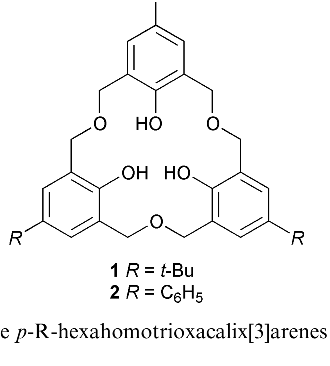
The use of [2.2.2]cryptand as a deprotonating agent during the synthesis of the mononuclear, monoanionic, uranyl ion complexes of *p*-R-hexahomotrioxacalix[3]arenes (R = *tert*-butyl, phenyl) results in the formation of supramolecular assemblies, which have been characterized by their crystal structures and ^{1}H NMR spectra in solution. In the 1 : 1 complex–cryptand assembly, the *endo* monoprotonated cryptand has its ammonium end embedded in the complex cavity, whereas, in the 2 : 1 complexes, the *endo* diprotonated cryptand is encapsulated in a "sandwich" mode by two complexes with convergent concave surfaces. The latter complexes are the first examples of the use of [2.2.2]cryptand as a "connector" to build calixarene supramolecular systems. The importance of cation–π interactions in this assembling process is discussed.

The crystal structures of the polyphenoxide uranyl complexes of calixarenes, homooxa- and homoazacalixarenes, which, following the work of Harrowfield *et al.*,[1,2] we have investigated in recent years, evidence several interesting new features, such as the propensity of large macrocycles to promote the formation of polyuranate clusters,[3,4] the peculiar, zwitterionic, complexation mode of homoazacalixarenes[5] or the existence of uranyl trigonal coordination.[6] In the course of this work, it appeared also that it is possible to build supramolecular assemblies from such systems by either of two routes. The first uses the hydrogen bond acceptor property of the uranyl oxo atoms, which has been shown to result in dimerisation of the tri-uranate complex of *p-tert*-butylhexahomotrioxacalix[6]arene, thus highlighting the importance of this ion in supramolecular chemistry.[7] The second method was recently evidenced from the study of the homooxacalixarene complexes obtained with different primary, secondary and tertiary amines as deprotonating agents.[8,9] The supramolecular assembly in this last case results from inclusion of ammonium ions, and possibly solvent molecules, in the macrocycle cavity and the formation of an extended hydrogen bonding pattern, particularly so in the case of primary and secondary amines.[10] Whereas the first case originates from a well-defined peculiarity of the uranyl ion which can be used to design new supramolecular systems, the second, involving multi-species hydrogen bonding, may be somewhat unpredictable. A third way can be devised, which exploits a dication able to bridge two anionic complex molecules by hydrogen bonds, cation–π interactions or other kinds of interactions. A likely candidate for such a purpose is the tertiary diamine [2.2.2]cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosan, denoted [222] in the following). This molecule can be doubly protonated and hence be present in a 1 : 2 stoichiometry with a monoanionic complex molecule such as those obtained with hexahomotrioxacalix[3]arenes.[6,8] Furthermore, it has a convenient size and geometry to be half-embedded in the cavity of some calixarenes and it is a potential hydrogen bond donor at both ends. We describe herein the synthesis and crystal structure of three uranyl complexes of *p*-R-hexahomotrioxacalix[3]arenes [R = *tert*-butyl (**1**), phenyl (**2**); Scheme 1] obtained in the presence of [222]. We have shown recently that this family of hexahomotrioxacalix[3]arenes is able to complex the uranyl ion equatorially giving either pseudo-trigonal or strongly distorted tetragonal or pentagonal coordination, depending on the number of coordinated ether atoms,[8] and the present results will further illustrate this point. To the best of our knowledge, the crystal structures reported herein are the first of supramolecular assemblies which unite macrocycles in the calixarene or homooxacalixarene families and [2.2.2]cryptand, although both are extensively investigated species in supramolecular chemistry.[11]

Experimental

Synthesis

[H222][UO$_2$(1 − 3H)] (3). A mixture of *p-tert*-butylhexahomotrioxacalix[3]arene **1**[12] (26 mg, 0.045 mmol) and [2.2.2]-cryptand (48 mg, 0.13 mmol) in MeOH (7 mL) was heated



1 *R* = *t*-Bu
2 *R* = C$_6$H$_5$

Scheme 1 The *p*-R-hexahomotrioxacalix[3]arenes under study.

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Table 1 Crystal data and structure refinement details

	3	4	5
Empirical formula	$C_{54}H_{82}N_2O_{14}U$	$C_{91}H_{134}N_2O_{24}U_2$	$C_{102}H_{104}N_2O_{22}U_2$
M/g mol^{-1}	1221.25	2116.06	2185.93
T/K	100(2)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	Pn	$P2_1/n$
a/Å	14.3837(6)	13.4667(7)	25.3546(11)
b/Å	20.2772(6)	39.338(2)	13.8369(9)
c/Å	21.5187(6)	18.4026(14)	28.0625(14)
α/°	66.410(2)	90	90
β/°	79.842(2)	93.062(4)	112.456(4)
γ/°	79.466(2)	90	90
V/Å^3	5617.5(3)	9734.9(10)	9098.6(8)
Z	4	4	4
μ/mm^{-1}	2.953	3.392	3.631
Reflections collected	39 075	54 920	54 783
Independent reflections	19 770	30 945	16 835
Observed reflections [$I > 2\sigma(I)$]	14 480	15 198	8352
Parameters refined	1289	2181	1153
R_{int}	0.055	0.088	0.087
R_1	0.040	0.086	0.072
wR_2	0.081	0.167	0.123

and stirred for 10 min, then uranyl acetate dihydrate (21 mg, 0.050 mmol) in MeOH (2 mL) was added dropwise. The obtained solution was heated for an additional 10 min and red–orange single crystals suitable for X-ray diffraction were collected after 4 days. Anal. calc. for $C_{54}H_{82}N_2O_{14}U$: C, 53.11; H, 6.77; N, 2.29; found: C, 52.97; H, 6.89; N, 2.36%.

[$H_2$222][UO_2(1 − 3H)]$_2$·CH_3OH·H_2O (4). A mixture of *p*-*tert*-butylhexahomotrioxacalix[3]arene **1** (29 mg, 0.050 mmol) and [2.2.2]cryptand (18 mg, 0.048 mmol) in MeOH (13 mL) was heated and stirred for 20 min, then uranyl acetate dihydrate (22 mg, 0.052 mmol) in MeOH (2 mL) was added dropwise. The obtained solution was heated and stirred for an additional 10 min and red–orange single crystals suitable for X-ray diffraction were collected after 3 days. Anal. calc. for $C_{91}H_{134}N_2O_{24}U_2$: C, 51.65; H, 6.38; N, 1.32; found: C, 51.85; H, 6.20; N, 1.46%.

[$H_2$222][UO_2(2 − 3H)]$_2$ (5). A mixture of *p*-phenylhexahomotrioxacalix[3]arene **2**[13] (32 mg, 0.050 mmol) and [2.2.2]-cryptand (19 mg, 0.050 mmol) in MeOH (15 mL) was heated and stirred for 15 min, then uranyl acetate dihydrate (23 mg, 0.054 mmol) in MeOH (2 mL) was added dropwise. A reddish precipitate immediately formed. Chloroform was added and the mixture was further heated and stirred to obtain a homogeneous solution from which, on slow evaporation, red–orange single crystals suitable for X-ray diffraction were collected after 10 days. Anal. calc. for $C_{102}H_{104}N_2O_{22}U_2$: C, 56.04; H, 4.80; N, 1.28; found: C, 55.81; H, 4.95; N, 1.43%.

Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer[14] using graphite-monochromated Mo-Kα radiation (λ 0.71073 Å). The crystals were introduced in glass capillaries with a protecting "Paratone" oil (Exxon Chemical, Ltd.) coating. The unit cell parameters were determined from ten frames, then refined on all data. A 180° φ-range was scanned with 2° steps during data collection, with the crystal-to-detector distance fixed to 28 mm. The data were processed with DENZO-SMN.[15] All structures were solved by direct methods with SHELXS-97[16] and subsequent Fourier-difference synthesis. The structures of **3** and **5** have been refined by full-matrix and that of **4** by blocked full-matrix least-squares on F^2 with SHELXL-97.[17] Absorption effects were corrected empirically with the program DELABS from PLATON.[18] In compound **3**, two *tert*-butyl groups were found to be disordered over two positions which have been refined with occupation factors constrained to sum to unity and some restraints on displacement parameters. In compound **4**, some restraints on bond lengths in *tert*-butyl groups, some parts of the [$H_2$222] cations and one methanol molecule have been applied, as well as some restraints on displacement parameters for several atoms of this large structure. Some voids in the three structures may indicate the presence of disordered, unresolved solvent molecules, as is frequently observed in such calixarene complexes. Ammonium protons were introduced as found on the Fourier-difference maps for compounds **3** and **5**, but they were not found in **4**. All other hydrogen atoms were introduced at calculated positions, except in the disordered parts and solvent molecules, when present. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (NH, CH, CH_2) or 1.5 (CH_3) times that of the parent atom. All non-hydrogen atoms were refined anisotropically, except the disordered ones in **3**. Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with SHELXTL.[19] All calculations were performed on a Silicon Graphics R5000 workstation.

CCDC reference numbers 181042–181044. See http://www.rsc.org/suppdata/nj/b2/b200734g/ for crystallographic data in CIF or other electronic format.

NMR measurements

^{1}H NMR spectra were recorded on a Bruker AC 300 spectrometer. CD_2Cl_2 and $CDCl_3$ were stored on activated molecular sieves (4 Å) and care was taken to minimize adventitious water during sample preparation.

Results and discussion

Complexes in the solid state

The asymmetric unit in the crystal structure of [H222][UO_2(1 − 3H)] **3** comprises two independent complex molecules, each with a monoprotonated cryptand counterion, as expected from the monoanionic nature of the uranyl

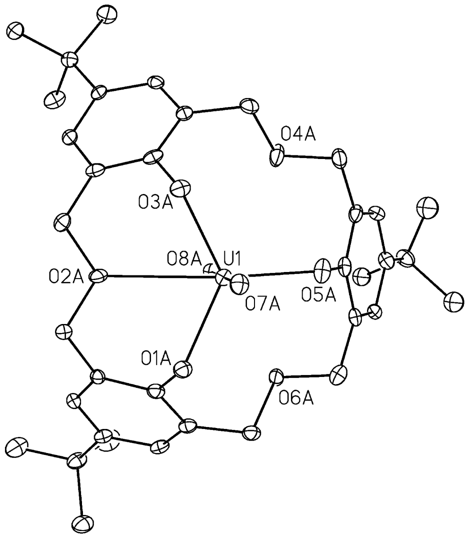


Fig. 1 View of the complex anion $[UO_2(\mathbf{1}-3H)]$ in **3** (unit A) with the oxygen atom labelling used throughout. Hydrogen atoms omitted for clarity. Only one position of the disordered *tert*-butyl group is represented. Ellipsoids are drawn at the 30% probability level.

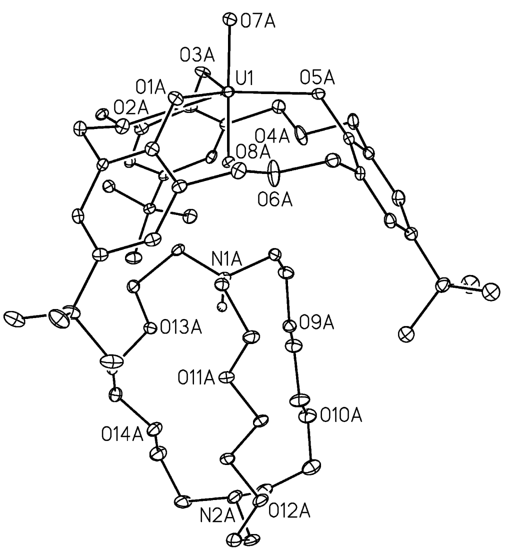


Fig. 2 View of the complex $[H222][UO_2(\mathbf{1}-3H)]$ **3** (unit A only). Hydrogen atoms omitted for clarity, except for that of the ammonium nitrogen atom. Only one position of the disordered *tert*-butyl group is represented. Ellipsoids are drawn at the 20% probability level.

complexes of **1**. The two complex assemblies, denoted A and B, are devoid of any crystallographic symmetry element and present slightly different coordination spheres around the uranyl ions (assembly A is shown in Fig. 1). In both complexes, the uranium atom is bound to two axial oxo atoms, with the usual geometry, and to the three phenoxide oxygen atoms, with a mean U–O bond length of 2.23(1) Å (including both molecules), usual in such compounds[8] (Table 2). However, in complex A, only one ether oxygen atom can be considered as bound to the uranium atom, with a bond length U(1)–O(2A) of 2.848(4) Å, whereas, in complex B, two ether oxygen atoms are possibly bound [U(2)–O(2B) 2.873(4), U(2)–O(6B) 2.871(4) Å], *i.e.* atom U(1) is in a distorted octahedral environment and U(2) is in a distorted pentagonal bipyramidal environment. We have previously pointed out some geometric features of the hexahomotrioxacalix[3]arene molecules which vary according to the number of coordinated ether atoms [O···O distances, O–U–O angles, distances between O(ether) and the phenolic O_3 mean plane, planarity of the ether bridges].[8] The variations of these parameters previously put in evidence hold in the present case also, and will not be described in further detail. Table 3 reports some of these parameters, as well as the dihedral angles between the phenolic rings and the O_3 mean plane, which are typical of a rather deep and regular *cone* conformation. The singly-protonated [H222] cation is located, in both assemblies A and B, so that the end with the protonated nitrogen atom is included in the homooxacalixarene cavity, as depicted in Fig. 2. It has been shown that, although the "out–out" conformation in doubly protonated [222] is less stable than the "in–in" one, it could be stabilized in the solid state by the presence of an external hydrogen bond acceptor.[20] However, contrary to our expectation of *exo* protonation of the ammonium moiety in the present case, due to the possibility of an ammonium···oxo hydrogen bond (as frequently observed in calixarene/homooxacalixarene complexes),[2] *endo* protonation is observed, resulting in an "in" conformation of the included end of the cryptand. The inwardly directed proton of the ammonium group is probably involved in an intraionic trifurcated hydrogen bonding interaction with the three nearer ether oxygen atoms (Table 4), as is usual. The amine end of the cryptand is also in the "in" conformation in both molecules, resulting in N···N separations within each molecule of 6.787(7) and 6.861(6) Å, *i.e.* the same as or slightly shorter than in the neutral cryptand (6.87 Å).[21] However, the conformation is somewhat different in the two halves of each cryptand, as indicated by the O···O separations which delineate the so-called "triangular faces"[20] [O(9)···O(11)···O(13) and O(10)···O(12)···O(14)]. These distances range from 3.443(5) to 3.693(5) Å [mean value 3.6(1) Å, including both molecules A and B; standard deviation in brackets] for the "face" closer to the ammonium end and from 4.079(5) to 4.670(5) [mean value 4.4(3)] Å for the other "face", in agreement with the presence of a trifurcated hydrogen bond interaction in the former case. The N–C–C–O torsion angles are in the range 55–76°, but, in each molecule, two O–C–C–O torsion angles are *anti* (170–179°, the third angles are 79 and 85°), resulting in the central parts of two ether chains being nearly planar. Some C–O–C–C torsion angles also deviate strongly from 180° and one of them, in molecule A, is nearly a *gauche* angle (86°). Surprisingly enough, a search of the Cambridge Structural Database (version 5.22)[22] gives no example of a monoprotonated [2.2.2]cryptand for comparison. In spite of the absence of an ammonium···oxo hydrogen bond, the protonated cryptand assumes the expected position, likely held by cation–π interactions[8,23] and weak CH–π interactions[24] involving the carbon atoms nearer to the nitrogen atom [shortest $C\cdots C_{arom}$ distance 3.45 Å, comparable to those previously found for other ammonium counter-ions;[8] shortest C···X distance (where X is an aromatic ring centroid) 3.54 Å; shortest N···X distance 4.57 Å]. An electrostatic cation/anion effect should also be considered in the overall energetics of the complex and it should be noted that, in both assemblies A and B, the ammonium, and not the amine group, is included in the cavity. As a result, this arrangement leaves one of the amine groups of the cryptand available for further protonation and inclusion.

On decreasing the molar ratio of cryptand with respect to uranyl-homooxacalixarene during the synthesis, a second compound, $[H_2222][UO_2(\mathbf{1}-3H)]_2\cdot CH_3OH\cdot H_2O$ (**4**), is obtained, in which two monoanionic complex molecules encapsulate a doubly protonated cryptand. The repeat unit comprises two such assemblies (corresponding to homooxacalixarenes A–B and C–D). One of the two assemblies (A–B) is shown in Fig. 3. In the three first complex anions, A, B and C, the uranium atoms [U(1), U(2) and U(3)] are in distorted octahedral environments, as in molecule A of compound **1**, whereas U(4) is better described as being in a trigonal bipyramidal environ-

Table 2 Environment of the uranium atom in compounds **3**–**5**: selected distances (Å) and angles (°)

	U–O(oxo)		U–O(phenoxide)		U–O(ether)		O–U–O	
3	U(1)–O(7A)	1.793(4)	U(1)–O(1A)	2.220(4)	U(1)–O(2A)	2.848(4)	O(7A)–U(1)–O(8A)	178.5(2)
	U(1)–O(8A)	1.772(3)	U(1)–O(3A)	2.204(3)	U(1)···O(4A)	3.449(5)	O(1A)–U(1)–O(2A)	68.0(1)
			U(1)–O(5A)	2.236(4)	U(1)···O(6A)	3.217(5)	O(2A)–U(1)–O(3A)	66.6(1)
							O(1A)–U(1)–O(3A)	127.9(1)
							O(3A)–U(1)–O(5A)	113.5(1)
							O(5A)–U(1)–O(1A)	118.0(1)
	U(2)–O(7B)	1.784(4)	U(2)–O(1B)	2.231(3)	U(2)–O(2B)	2.873(4)	O(7B)–U(2)–O(8B)	176.9(2)
	U(2)–O(8B)	1.776(3)	U(2)–O(3B)	2.241(4)	U(2)···O(4B)	3.697(4)	O(1B)–U(2)–O(2B)	66.5(1)
			U(2)–O(5B)	2.226(3)	U(2)–O(6B)	2.871(4)	O(2B)–U(2)–O(3B)	68.9(1)
							O(1B)–U(2)–O(3B)	128.9(1)
							O(3B)–U(2)–O(5B)	104.2(1)
							O(5B)–U(2)–O(6B)	68.4(1)
							O(6B)–U(2)–O(1B)	65.0(1)
							O(5B)–U(2)–O(1B)	125.9(1)
4	U(1)–O(7A)	1.78(1)	U(1)–O(1A)	2.22(1)	U(1)–O(2A)	2.82(1)	O(7A)–U(1)–O(8A)	176.1(7)
	U(1)–O(8A)	1.83(1)	U(1)–O(3A)	2.22(1)	U(1)···O(4A)	3.67(1)	O(1A)–U(1)–O(2A)	67.5(4)
			U(1)–O(5A)	2.23(1)	U(1)···O(6A)	3.18(1)	O(2A)–U(1)–O(3A)	70.8(5)
							O(1A)–U(1)–O(3A)	132.9(5)
							O(3A)–U(1)–O(5A)	109.2(5)
							O(5A)–U(1)–O(1A)	117.5(5)
	U(2)–O(7B)	1.76(2)	U(2)–O(1B)	2.20(2)	U(2)–O(2B)	2.79(2)	O(7B)–U(2)–O(8B)	178.2(8)
	U(2)–O(8B)	1.80(2)	U(2)–O(3B)	2.19(1)	U(2)···O(4B)	3.53(2)	O(1B)–U(2)–O(2B)	69.5(5)
			U(2)–O(5B)	2.22(2)	U(2)···O(6B)	3.22(2)	O(2B)–U(2)–O(3B)	69.3(4)
							O(1B)–U(2)–O(3B)	132.1(7)
							O(3B)–U(2)–O(5B)	109.8(6)
							O(5B)–U(2)–O(1B)	117.5(7)
	U(3)–O(7C)	1.77(2)	U(3)–O(1C)	2.17(2)	U(3)–O(2C)	2.79(2)	O(7C)–U(3)–O(8C)	177.9(8)
	U(3)–O(8C)	1.80(1)	U(3)–O(3C)	2.27(2)	U(3)···O(4C)	3.42(2)	O(1C)–U(3)–O(2C)	67.8(6)
			U(3)–O(5C)	2.24(1)	U(3)···O(6C)	3.36(2)	O(2C)–U(3)–O(3C)	70.2(5)
							O(1C)–U(3)–O(3C)	133.3(6)
							O(3C)–U(3)–O(5C)	113.8(5)
							O(5C)–U(3)–O(1C)	112.6(6)
	U(4)–O(7D)	1.80(2)	U(4)–O(1D)	2.20(2)	U(4)···O(2D)	3.03(2)	O(7D)–U(4)–O(8D)	178.0(7)
	U(4)–O(8D)	1.81(1)	U(4)–O(3D)	2.26(2)	U(4)···O(4D)	3.13(2)	O(1D)–U(4)–O(3D)	122.1(6)
			U(4)–O(5D)	2.21(2)	U(4)···O(6D)	3.39(2)	O(3D)–U(4)–O(5D)	118.7(6)
							O(5D)–U(4)–O(1D)	118.5(6)
5	U(1)–O(7A)	1.775(7)	U(1)–O(1A)	2.227(8)	U(1)–O(2A)	2.609(8)	O(7A)–U(1)–O(8A)	177.0(4)
	U(1)–O(8A)	1.768(8)	U(1)–O(3A)	2.203(8)	U(1)···O(4A)	3.478(9)	O(1A)–U(1)–O(2A)	71.1(3)
			U(1)–O(5A)	2.228(8)	U(1)···O(6A)	3.692(9)	O(2A)–U(1)–O(3A)	70.0(3)
							O(1A)–U(1)–O(3A)	139.3(3)
							O(3A)–U(1)–O(5A)	112.6(3)
							O(5A)–U(1)–O(1A)	108.1(3)
	U(2)–O(7B)	1.776(7)	U(2)–O(1B)	2.222(8)	U(2)–O(2B)	2.658(9)	O(7B)–U(2)–O(8B)	178.7(4)
	U(2)–O(8B)	1.766(6)	U(2)–O(3B)	2.234(9)	U(2)···O(4B)	3.132(8)	O(1B)–U(2)–O(2B)	73.0(3)
			U(2)–O(5B)	2.217(7)	U(2)···O(6B)	3.594(8)	O(2B)–U(2)–O(3B)	68.0(3)
							O(1B)–U(2)–O(3B)	136.0(3)
							O(3B)–U(2)–O(5B)	116.9(3)
							O(5B)–U(2)–O(1B)	105.9(3)

ment.[6,8] Some geometric details are given in Tables 2 and 3, and, being in accord with previous results, they will not be discussed further. In both assemblies, two complex anions face each other with their upper rims, or concave sides, so as to include the [H$_2$222] dications, with dihedral angles between the O$_3$ planes of 15.4(7) and 2.4(8)° within the A–B and C–D assemblies, respectively. The ammonium hydrogen atoms were not found in **4**, but the "in–in" conformation of both ends of each cryptand is obvious and intraionic trifurcated hydrogen bonds can be inferred from the N···O distances. As a result, the N···N separations [N(1)···N(2) 5.84(3), N(3)···N(4) 6.29(3) Å] are significantly shorter than in compound **3**. The edges of the "triangular faces" are in the range 3.85(3)–4.68(3) [mean value 4.2(3)] Å in the first unit and 3.56(3)–4.13(3) [mean value 3.8(2)] Å in the second. The values in the last cation are close to those in the protonated half of [H222] in compound **3**, whereas they are larger in the first cation. This difference can be ascribed to the presence in the first [H$_2$222] cation (A–B assembly) of a central water molecule [O(15)], possibly hydrogen bonded to the ammonium groups and, with some disorder on hydrogen atoms, to the six ether oxygen atoms (Table 4). The A–B assembly can thus be viewed as an example of double host–guest inclusion. To the best of our knowledge, no other structure of water-containing [2.2.2]cryptand has ever been reported. This cryptand thus assumes a less elongated shape than the empty one, in agreement with its shorter N···N separation. As a possible consequence, the U···U separation in the A–B unit [15.662(2) Å] is slightly shorter than that in C–D [16.053(2) Å]. The differences in conformation between the two cryptands are also apparent from the torsion angle values. In the first unit, the N–C–C–O, O–C–C–O and C–O–C–C torsion angles are in the range 41–78, 61–67 and 139–179°, respectively, whereas, in the second unit, three N–C–C–O angles are much distorted

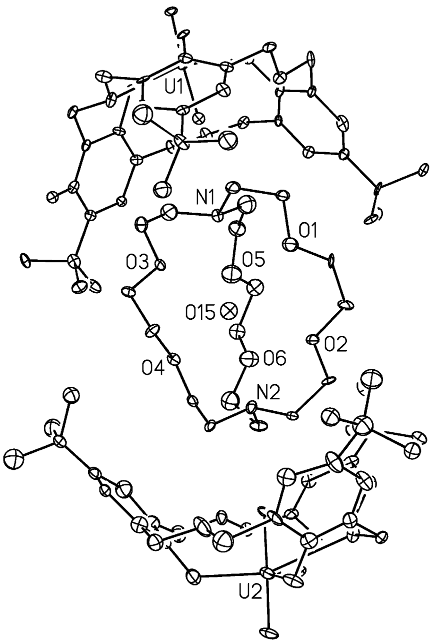


Fig. 3 View of one of the two independent $[H_2222][UO_2(\mathbf{1}-3H)]_2$ units in **4**. Solvent molecules and hydrogen atoms omitted for clarity. Ellipsoids are drawn at the 10% probability level.

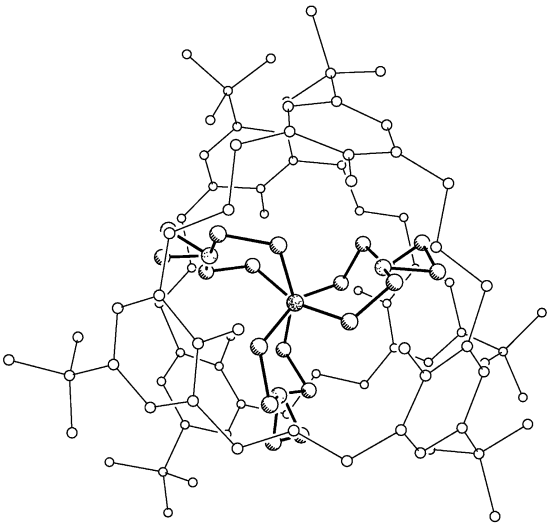


Fig. 4 View of one of the two independent $[H_2222][UO_2(\mathbf{1}-3H)]_2$ units in **4** along the cryptand N···N axis. Uranyl ions, solvent molecules and hydrogen atoms omitted for clarity. The calixarene frameworks are shown as small spheres and thin lines and the encapsulated cryptand as large spheres and bold lines.

(10–15°, the other in the range 40–70°), the O–C–C–O and C–O–C–C torsion angles being in the ranges 82–95 and 136–179°, respectively. As in compound **3**, the protonated cryptands in **4** are possibly held in the macrocycle cavity by cation–π interactions and by weak CH–π interactions involving the carbon atoms nearer to the nitrogen atoms [shortest $C\cdots C_{arom}$ distance 3.53 Å; shortest C···X (centroid) distance 3.56 Å; shortest N···X distance 4.54 Å] besides electrostatic anion–cation interactions. As illustrated in Fig. 4, the two homooxacalixarene molecules present a staggered arrangement when viewed along the cryptand main axis, with rotation angles of about 19 and 25°, respectively, in the two assemblies.

As a further step, the hexahomotrioxacalix[3]arene **2** with phenyl substituents in the *para* position, and hence a potentially deeper cavity, was used, resulting in the compound $[H_2222][UO_2(\mathbf{2}-3H)]_2$ (**5**), represented in Fig. 5. The overall features of this complex are analogous to those of compound **4**. The asymmetric unit contains one assembly made up of two anionic $[UO_2(\mathbf{2}-3H)]$ complexes and one encapsulated $[H_2222]$ dicationic species. The uranium atoms are in distorted octahedral environments, with unremarkable geometric parameters. The dihedral angle between the O_3 mean planes of the two macrocycles, [23.7(4)°] indicates a more important tilt between the two anions than in compound **4**. As in the pre-

Table 3 Ligand geometry in compounds **3**–**5**: selected distances (Å) and dihedral angles between the mean plane O_3, defined by the three phenoxide oxygen atoms, and the aromatic rings φ(*i*) [associated to O(*i*)] (°)

	O(phenol)···O(phenol)		O(ether)···O_3		φ(*i*)–O_3	
3	O(1A)···O(3A)	3.974(5)	O(2A)	1.187(6)	φ(1A)	55.2(2)
	O(3A)···O(5A)	3.712(5)	O(4A)	1.585(7)	φ(2A)	51.7(1)
	O(1A)···O(5A)	3.819(6)	O(6A)	1.516(7)	φ(3A)	52.9(1)
	O(1B)···O(3B)	4.034(5)	O(2B)	1.150(6)	φ(1B)	59.8(1)
	O(3B)···O(5B)	3.524(5)	O(4B)	1.773(6)	φ(2B)	54.2(1)
	O(1B)···O(5B)	3.970(5)	O(6B)	1.216(6)	φ(3B)	50.3(2)
4	O(1A)···O(3A)	4.07(2)	O(2A)	1.13(2)	φ(1A)	54.2(5)
	O(3A)···O(5A)	3.62(2)	O(4A)	1.83(2)	φ(2A)	51.0(4)
	O(1A)···O(5A)	3.80(2)	O(6A)	1.49(2)	φ(3A)	53.0(6)
	O(1B)···O(3B)	4.01(2)	O(2B)	1.21(2)	φ(1B)	54.9(8)
	O(3B)···O(5B)	3.60(2)	O(4B)	1.65(3)	φ(2B)	49.3(5)
	O(1B)···O(5B)	3.78(3)	O(6B)	1.58(3)	φ(3B)	45.6(7)
	O(1C)···O(3C)	4.07(2)	O(2C)	1.06(3)	φ(1C)	53.8(6)
	O(3C)···O(5C)	3.78(2)	O(4C)	1.63(3)	φ(2C)	58.8(5)
	O(1C)···O(5C)	3.66(2)	O(6C)	1.63(2)	φ(3C)	55.6(7)
	O(1D)···O(3D)	3.90(2)	O(2D)	1.30(3)	φ(1D)	52.8(4)
	O(3D)···O(5D)	3.84(2)	O(4D)	1.50(3)	φ(2D)	50.0(7)
	O(1D)···O(5D)	3.78(2)	O(6D)	1.50(3)	φ(3D)	51.5(7)
5	O(1A)···O(3A)	4.15(1)	O(2A)	0.71(1)	φ(1A)	60.9(3)
	O(3A)···O(5A)	3.69(1)	O(4A)	1.64(1)	φ(2A)	55.4(3)
	O(1A)···O(5A)	3.61(1)	O(6A)	1.91(1)	φ(3A)	51.0(3)
	O(1B)···O(3B)	4.13(1)	O(2B)	0.94(1)	φ(1B)	60.0(3)
	O(3B)···O(5B)	3.79(1)	O(4B)	1.44(1)	φ(2B)	54.7(3)
	O(1B)···O(5B)	3.54(1)	O(6B)	1.73(1)	φ(3B)	44.4(4)

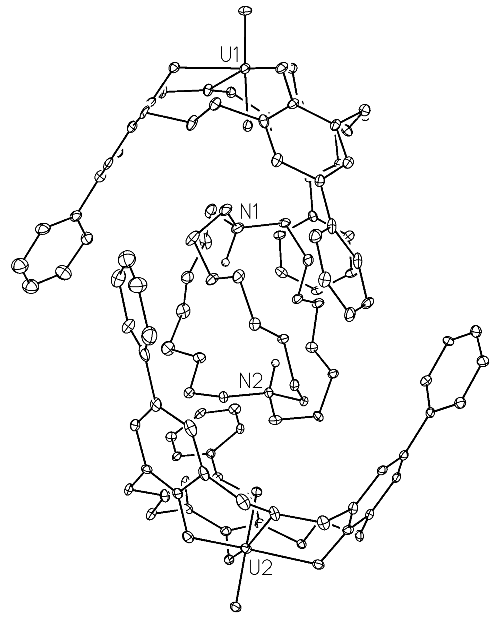


Fig. 5 View of the complex $[H_2222][UO_2(\mathbf{2}-3H)]_2$ (**5**). Hydrogen atoms omitted for clarity, except for those of the ammonium nitrogen atoms. Ellipsoids are drawn at the 10% probability level.

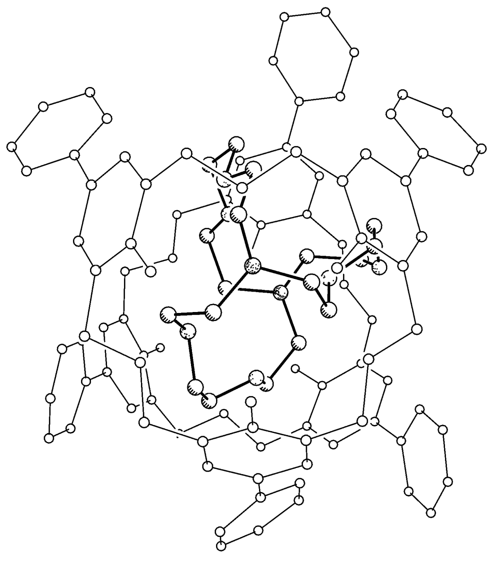


Fig. 6 View of the complex $[H_2222][UO_2(\mathbf{2}-3H)]_2$ (**5**). Uranyl ions and hydrogen atoms omitted for clarity. The calixarene frameworks are shown as small spheres and thin lines and the encapsulated cryptand as large spheres and bold lines.

vious structures, *endo* protonation of [222] is observed, resulting in the "in–in" conformation at both ends. However, the conformation of the cryptand is greatly distorted. The ammonium nitrogen atom N(1) is likely involved in a trifurcated hydrogen bond. More surprisingly, N(2) possibly forms a hydrogen bond with the nearer ether oxygen atoms O(4) and O(6) [O(2) being in an unsuitable geometry, in spite of a N(2)···O(2) distance of 2.82(1) Å] and also with the atom O(5), which pertains to the other half of the molecule. The N···N separation [5.25(1) Å] is shorter than in compounds **3** and **4**, as a result of the different conformation, and, partly as a consequence, the U(1)···U(2) separation [14.7598(9) Å] is shorter than its counterparts in compound **4**. The edges of the "triangular faces" are in the ranges 3.75(1)–4.00(1) [mean value 3.9(1)] Å for the end associated to N(1) and 4.32(1)–4.52(1) [mean value 4.4(1)] Å for the end associated to N(2). The N–C–C–O and O–C–C–O torsion angles are in the usual ranges, 41–69 and 61–65°, respectively, but three C–O–C–C torsion angles assume *gauche* geometries (70–81°, the other values lie in the range 155–179°). In the resulting geometry, the two N–H bonds are far from being co-axial. The $[H_2222]$ cation in **5** is possibly held in the macrocycle cavity by the same interactions as considered for compounds **3** and **4**, but the presence of the aromatic *p*-substituents possibly increases the importance of cation–π and CH–π interactions. Numerous short contacts exist between the cryptand and both the phenolic rings and the phenyl substituents: the shortest $C\cdots C_{arom}$ contact [3.23 Å] involves the second carbon atom of an ether chain and a carbon atom of a phenyl ring, whereas the shortest C···X (centroid) contact [3.48 Å] is between the first carbon atom of a chain and a phenolic ring and the shortest N···X distance [4.57 Å] also involves a phenolic ring. As can be seen in Fig. 6, the two homooxacalixarene molecules are staggered, with a larger rotation angle than in compound **4**. Due to the large tilt between the two macrocyclic mean planes, it is probably inadvisable to calculate the angle of rotation between the

Table 4 Hydrogen bonding geometry in compounds **3**–**5**: selected distances (Å) and angles (°)

3	N(1A)···O(9A)	2.806(6)	N(1A)–H(1A)	0.80	H(1A)···O(9A)	2.40	N(1A)–H(1A)···O(9A)	112.3
	N(1A)···O(11A)	2.712(5)			H(1A)···O(11A)	2.22	N(1A)–H(1A)···O(11A)	119.9
	N(1A)···O(13A)	2.768(6)			H(1A)···O(13A)	2.29	N(1A)–H(1A)···O(13A)	118.6
	N(1B)···O(9B)	2.801(5)	N(1B)–H(1B)	1.01	H(1B)···O(9B)	2.23	N(1B)–H(1B)···O(9B)	114.3
	N(1B)···O(11B)	2.762(6)			H(1B)···O(11B)	2.22	N(1B)–H(1B)···O(11B)	112.4
	N(1B)···O(13B)	2.722(5)			H(1B)···O(13B)	2.20	N(1B)–H(1B)···O(13B)	110.6
4[a]	N(1)···O(1)	2.74(3)	N(2)···O(2)	2.92(2)	N(3)···O(7)	2.86(3)	N(4)···O(8)	2.76(3)
	N(1)···O(3)	2.74(2)	N(2)···O(4)	3.04(2)	N(3)···O(9)	2.74(3)	N(4)···O(10)	2.86(3)
	N(1)···O(5)	2.87(3)	N(2)···O(6)	3.05(3)	N(3)···O(11)	2.64(3)	N(4)···O(12)	2.74(3)
	N(1)···O(15)	2.89(2)	N(2)···O(15)	2.97(2)				
	O(15)···O(1)	2.93(2)	O(15)···O(2)	2.97(2)				
	O(15)···O(3)	2.79(2)	O(15)···O(4)	2.74(2)				
	O(15)···O(5)	2.73(2)	O(15)···O(6)	2.89(2)				
5	N(1)···O(1)	2.94(2)	N(1)–H(1)	1.16	H(1)···O(1)	2.22	N(1)–H(1)···O(1)	116.7
	N(1)···O(3)	2.72(2)			H(1)···O(3)	2.21	N(1)–H(1)···O(3)	103.2
	N(1)···O(5)	2.94(1)			H(1)···O(5)	2.62	N(1)–H(1)···O(5)	94.3
	N(2)···O(4)	2.76(1)	N(2)–H(2)	1.05	H(2)···O(4)	2.54	N(2)–H(2)···O(4)	90.9
	N(2)···O(5)	3.24(1)			H(2)···O(5)	2.21	N(2)–H(2)···O(5)	164.9
	N(2)···O(6)	2.81(1)			H(2)···O(6)	2.32	N(2)–H(2)···O(6)	107.0

[a] Hydrogen atoms not found.

two complex anions along the cryptand main axis (which is itself very badly defined in this case), but this angle appears to be closer than in compound **4** to the ideal value of 60° necessary for minimization of steric interactions between the phenyl groups (the inter-macrocycle phenyl$\cdots$phenyl contacts are rather long, the shortest one being 3.96 Å). The cryptand thus appears more perfectly enveloped than it is in compound **4** and the assembly more compact, in spite of the larger *p*-substituents.

Complexes in solution

An investigation has also been carried out on complexes **3**–**5** in $CDCl_3$ solution. On the basis of the ^{1}H NMR spectra at 298 K, shown in Fig. 7, the same gross composition as observed in the crystal can be determined in solution, although the complexes are apparently highly symmetric, with no evidence of varying coordination of the uranyl ion or of differences in the branches of the protonated cryptand. Analogous to reports using simpler amines as deprotonating agents,[8] the geminal coupling for the $ArCH_2OCH_2Ar$ protons indicates that the ligand is in an enforced *cone* conformation, while there is no evidence of geminal coupling for the methylene groups of the protonated base. The inclusion of the protonated cryptand in the aromatic cavity is supported by marked up-field shifts for the signals of the guest cation, the estimated effects being reported in Fig. 8. The effects are very strong for α-methylenes and decrease regularly on increasing the distance from the charged nitrogen atom. The effects in the β and, particularly, in the δ positions are larger for compound **5** than for compound **4**, clearly due to the additional shielding effect of the *p*-phenyl substituents. Freezing less symmetric forms of the complexes was attempted in the case of **3** and **5** through low temperature experiments in CD_2Cl_2, but no major change was observed down to 185 K. Interestingly, no evidence was obtained in the latter studies of the competition between two different forms of complexes that was observed with simpler amines.[8] In that case, the form featuring a well-included ammonium ion prevailed at room temperature, but was extensively replaced at low temperature by an apparently external complex in which the ammonium ion was hydrogen bonded to a phenoxide oxygen atom. The absence of the external form in the present case can actually be accommodated into a previously observed trend, since ions derived from tertiary and bulky amines appeared to be the least prone to exit the cavity.[8] Both steric hindrance to external hydrogen bonding and well-fitted inclusion of the protonated cryptand into the aromatic cavity can explain the apparent stability of the encapsulated complexes in solution at low temperature, but the required reorganization of the cryptand moiety from "in–in" to "out–out" or "out–in" conformations is also expected to handicap external hydrogen bonded complexes.

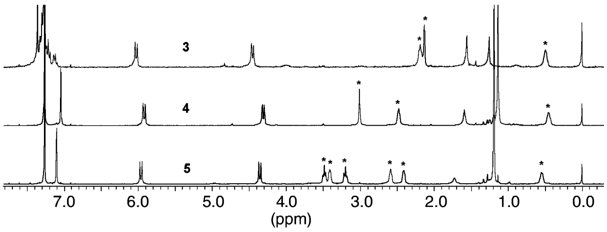
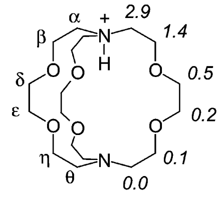
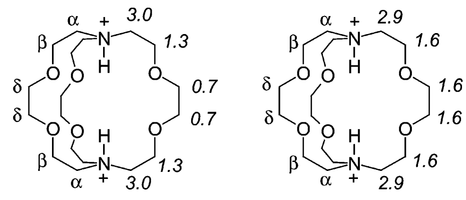


Fig. 7 ^{1}H NMR spectra of complexes **3**–**5** in $CDCl_3$ at 298 K. Peaks due to protonated [222] are marked with an asterisk.



in complex **3**



in complex **4** in complex **5**

Fig. 8 Estimated upfield shifts in the ^{1}H NMR spectra for protonated [222] on inclusion in the aromatic cavities of complexes **3**–**5**. In the case of compounds **4** and **5**, reference is made to chemical shifts reported for "in–in" diprotonated [222] in CH_3CN.[20] Unavailable chemical shifts for the "frozen" monoprotonated [222] have been estimated from data for diprotonated and non-protonated [222].[20]

Concluding remarks

We have shown that both nesting 1 : 1 : 1 and sandwich or capsular 2 : 2 : 1 complexes can be prepared from hexahomotrioxacalix[3]arenes, uranyl ions and [2.2.2]cryptand, the sandwich arrangement being obtained when a small rather than a large excess of the cryptand is used during the synthesis.

The association of two calixarene molecules with convergent concave surfaces encapsulating a guest was first recognized in the case of the *p*-*tert*-butylcalix[4]arene–anisole (2 : 1) complex, in which all components are neutral and the host–guest interactions are assumed to be of the CH_3 (host)$\cdots\pi$ (guest) type.[25] In this case, the two staggered macrocycles, located on a fourfold axis, are rotated by 43.0(2)° with respect to one another: this angle is larger than that observed in compound **4**, which has the same *p*-substituents, seemingly due to the smaller size of the guest bringing the two calixarenes in closer contact. Further examples of analogous sandwich encapsulation were reported later, involving calix[4]arene and small molecules[26] or even calix[5]arene or hexahomotrioxacalix[3]arene and C_{60}.[27] Recently, the strategy of holding two calix[4]arenes by using a "connector" guest was used in the design of koilates [non-covalently assembled linear array of hollow direceptor molecules (koilands) and connectors] and found its place in the subset of supramolecular chemistry which has been dubbed "molecular tectonics".[28] The connectors currently used are neutral linear molecules with two ends sufficiently far apart one from each other, such as hexadiyne, *p*-xylene or phenylpropyne (it may be noted that the distance between the terminal carbon atoms of these molecules, about 6.7, 5.8 and 6.9 Å, respectively, is close to the range of N$\cdots$N distances observed in the present compounds). Although the encapsulation of [2.2.2]cryptand or some of its cryptates (K^+, Sr^{2+}, Ba^{2+}) in a self-assembled hydrogen bonded molecular capsule has been achieved in solution,[11] the present results give, as far as we know, the first crystallographic characterization of sandwich inclusion of this cryptand by calixarenes.[29]

A remarkable peculiarity of compounds **4** and **5** is the simultaneous complexation of three cationic species (two uranyl ions and one protonated [222]) by two anionic hosts. In these systems, structural complementarity is twofold: first, between the homooxacalixarene and the uranyl ion, and second, between the complex thus formed and the included ammonium cation. Interestingly, these assemblies appear to be stable in solution, both in respect of their composition and their configuration, *i.e.* more stable than complexes obtained with simpler ammonium ions, that exit the cavity at low temperatures.[8] In spite of the absence of ammonium···oxo hydrogen bonds, due to the preferential *endo* protonation of [222], the directionality of the weak non-covalent interactions involved is sufficient to promote the planned "sandwich" encapsulation. Among these non-covalent interactions, the cation–π interaction[23] is likely to play a major role in the present case. The simple interaction between tetramethylammonium ion and benzene (for which classical hydrogen bonds, electrostatic cation–anion and π–π interactions are absent) has been particularly investigated from a theoretical point of view, a very recent work stressing the importance of dispersion interactions in addition to electrostatic cation–π interactions, while downplaying the importance of orbital interaction.[30] The above simple interaction is fairly strong, $-\Delta H^0 = 9.4$ kcal mol^{-1} in a vacuum,[31] and strong to very strong complexes between tetramethylammonium or larger related ions and neutral cyclophanes have been reported in solution.[23,32] Several analogous interactions may be present in complexes **3**–**5**, although an estimate of the relative strength of the various components is too difficult for the large cation with its peculiar charge distribution and the complex host system. As a simple criterion for the effectiveness of the interaction, distances between the centroids of the aromatic rings and charged nitrogen or α-carbon atoms can be considered, the distance of optimal interaction having been calculated to be about 4.2–4.7 Å for benzene and the nitrogen atom of tetramethylammonium ion in a vacuum.[30,33–35] On the other hand, in an analysis of 154 crystal structures in a study of the interaction between the $N(CH_3)_3R^+$ group and phenyl rings in proteins, a clustering of phenyl rings at about 4.5 Å from positive nitrogen atoms has been observed,[36] while several distances in the range 3.4–3.9 Å, comparable to those in the present compounds, have been found between α-carbon atoms and the centroids of aromatic rings in the crystal of a well-fitted complex between a neutral host and acetylcholine.[37] The shortest N···X distances in compounds **3**–**5** (where X is an aromatic ring centroid) are in the range 4.46–4.57 Å, *i.e.* they are in the range cited above for cation–π interactions. Several structures of assemblages comprising anionic calixarenes or homooxacalixarenes metal complexes and included primary, secondary and tertiary ammonium counter-ions have also been reported, but in most cases hydrogen bonding is superimposed to cation–anion and cation–π interactions to determine the strength and the geometry of the association.[8,9] Complexes of tetraalkylammonium cations with anionic calixarenes, which are relevant to the complexation of acetylcholine,[38] have also been reported and the existence of cation–π and CH–π interactions has been discussed in these cases. The overall anionic charge of the homooxacalixarene–UO_2 moieties in **3**–**5** and the importance of anion–cation interactions in assembling the sandwich capsules should be considered, but the cation does not face the phenoxide oxygen atoms in the lower rim of the host where the negative charge is mainly located. The actual close interaction of the overall anionic species with the cation is largely through the aromatic rings, *i.e.* rings more electron-rich than those of benzene, so that this interaction can be considered to somewhat merge with the cation–π interaction. CH–π interactions are expected to be less energetic,[39] moreover, in the presence of a cationic guest, they can barely be separated from the cation–π interactions considered above. In conclusion, although several interactions can contribute to the stabilization of the sandwich-encapsulated complexes, the cation–π interaction can be safely considered to be one of the most important; both the distances observed in the crystal and the shielding effects on the ^{1}H NMR spectra in solution indicating that the large moieties of the guest cations are quite close to the aromatic rings of the host.

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