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A Tetrahomodioxacalix[6]arene as a Ditopic Ligand for Uranyl Ions with Carbonate or Carbamate Bridges

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The first crystal structures of a *p-tert*-butyltetrahomodioxacalix[6]arene comprising two tri-phenolic subunits separated by two ether bridges and two of its complexes with uranyl ions are reported. The doubly deprotonated macrocycle assumes a much elongated, *cone*-like conformation including two organic species. Two binuclear uranyl complexes are described. In both, each cation is bound to the three phenoxide oxygen atoms of a tri-phenolic subunit and to a central, bridging, carbonate or carbamate ion. The formation of the latter ions from the amines used as bases is discussed.

Keywords: Uranyl ion; Calixarenes; Homooxacalixarenes; Crystal structure

INTRODUCTION

The study of the chemistry and crystal structures of poly-aryloxide uranyl complexes involving calixarenes and homooxacalixarenes is presently a highly documented domain [1,2]. However, among other interesting developments, the use of uranyl complexes with these ligands to build supramolecular assemblages, which appears to be a promising field, remains to be more fully investigated. Several approaches may be used towards this goal. The simplest one, which has been shown to give polyuranate clusters, exploits the poly-metallic complexing ability of large calixarenes [1–3]. A second approach makes use of the oxo-basicity of the uranyl ion and in particular of its ability to act as a hydrogen bond acceptor [4]. Finally, the inclusion of ammonium counter-cations in the calixarene cavity can be used in conjunction with hydrogen bonding to generate various assemblages, particularly so for primary or secondary amines which are able to give divergent hydrogen bonds [5,6]. We have also shown recently that the diamine [2.2.2]cryptand can be included by each of its two ends in two facing cavities of uranyl complexes of hexahomotrioxacalix[3]arene to give sandwich assemblages [7].

The development of such areas requires a thorough characterisation of the crystal structures of uranyl complexes with a large array of calixarenes and homooxacalixarenes and in the presence of various amines. Unfortunately, the crystallisation of such species, and particularly of those involving large macrocycles, is often a difficult step that hampers such an investigation. By contrast with its positional isomer consisting of a di- and a tetra-phenolic subunit linked by two ether bridges, which has been structurally characterised both as a triethylammonium and a 1:1 uranyl ion complex [3], the more symmetric *p-tert*-butyltetrahomodioxacalix[6]arene (represented in Scheme 1 and denoted LH_6 hereafter) appears to constitute a particularly recalcitrant case {in the notation based on the number of atoms in the bridges, LH_6 and its isomer cited above, denoted $L'H_6$ hereafter, correspond to [3.1.1.3.1.1]- and [3.1.3.1.1.1]homooxacalixarenes, respectively [8]}. The difficulty with LH_6 arises from its high insolubility in usual solvents, which makes it extremely problematic to obtain in single crystal form. This is more unfortunate as this molecule, with its two tri-phenolic subunits, is a potentially interesting ditopic ligand. The size of both LH_6 and $L'H_6$ is intermediate between those of calix[7]arene and calix[8]arene [3]. Calix[8]arene

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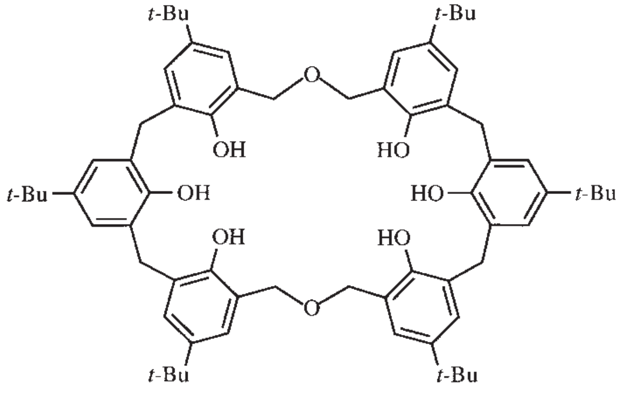


SCHEME 1 *p-tert*-Butyltetrahomodioxacalix[6]arene, LH_6.

accommodates two uranyl ions [1,2] whereas calix[7]arene can accommodate one or two depending on experimental conditions [9,10]. $L'H_6$ adopts a very distorted conformation upon uranyl complexation with formation of a mononuclear complex. In order to determine the effect of a different location of the two ether bridges on the stoichiometry and geometry of the complex formed, the overall size of the macrocycle being kept constant, we insisted particularly on crystallizing uranyl complexes of LH_6 and for this we used various combinations of solvents and counter-ions. The peculiar resulting crystal structures, albeit of rather low quality, are reported herein.

EXPERIMENTAL

Synthesis

The *p-tert*-butyltetrahomodioxacalix[6]arene LH_6 was synthesised as previously reported [11].

$[pyrC(CH_3)NH_2]_2[LH_4]\cdot 0.5pyrC(CH_3)NH\cdot 5CH_3CN$ **1** (pyr = pyrrolidine; $pyrC(CH_3)NH$ = *N*,*N*-tetramethyleneacetamidine): pyrrolidine (80 mg, 1.1 mmol) was added dropwise to a stirred and heated mixture of LH_6 (35 mg, 0.034 mmol) in acetonitrile (5 ml). Heating of the readily obtained homogeneous solution was continued for a few minutes and colourless single crystals of **1** suitable for X-ray crystallography formed after 24 h.

$[Hpyr]_4[(UO_2)_2L(CO_3)]\cdot pyr\cdot 2H_2O$ **2**: a mixture of LH_6 (18 mg, 0.017 mmol) and pyrrolidine (200 mg, 2.8 mmol) in MeOH (10 ml) was stirred and heated for 10 min. On addition of acetonitrile (1 ml), partial ligand dissolution was observed while a homogeneous orange solution was observed after dropwise addition of uranyl acetate dihydrate (19 mg, 0.045 mmol) in MeOH (3 ml) and further heating and stirring for 10 min. A yellowish powder that precipitated on standing was filtered off after 24 h and orange single crystals of **2** suitable for X-ray crystallography were obtained on slow evaporation of the solution.

$[BuNH_3]_3[(UO_2)_2L(BuNHCOO)]\cdot 3BuNH_2$ **3**: a mixture of LH_6 (18 mg, 0.017 mmol), butylamine (500 mg, 6.8 mmol) and uranyl acetate dihydrate (18 mg, 0.042 mmol) in MeOH (12 ml) was stirred and heated for 20 min to obtain a homogeneous orange solution. After 24 h, the yellowish precipitate was filtered off and orange single crystals of **3** suitable for X-ray crystallography were obtained on slow evaporation of the solution.

Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer [12] using graphite-monochromated Mo Kα radiation (0.71073 Å). The crystals were introduced in Lindemann glass capillaries with a protecting "Paratone" oil (Exxon Chemical Ltd.) coating. The unit cell parameters were determined from the reflections collected on ten frames and were then refined on all data. The data were processed with DENZO-SMN [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]. Absorption effects in compounds **2** and **3** were empirically corrected with the program DELABS from PLATON [16]. Special details for each compound are as follows:

Compound **1**: One *tert*-butyl group and the pyrrolidine part of one protonated *N*,*N*-tetramethyleneacetamidine molecule have been found disordered over two sites which have been refined with occupancy parameters constrained to sum to unity. Another *N*,*N*-tetramethyleneacetamidine molecule is disordered around a symmetry centre. All non-hydrogen atoms were refined with anisotropic displacement parameters, except those of the disordered *tert*-butyl group and the disordered part of the *N*,*N*-tetramethyleneacetamidine molecule. Some constraints on bond lengths, angles and displacement parameters have been applied to the counter-ions and some solvent molecules. The protons bound to phenolic oxygen atoms have been found on the Fourier-difference map. Those bound to nitrogen atoms have not been found. Those of the $pyrC(CH_3)NH_2$ cations have been introduced at calculated positions, but not the one of the neutral $pyrC(CH_3)NH$.

Compound **2**: All non-hydrogen atoms were refined with anisotropic displacement parameters, except two carbon atoms in the pyrrolidine molecules, which behave badly on refinement. Some constraints on bond lengths and displacement parameters have been applied in the *tert*-butyl groups and pyrrolidine molecules. The protons bound to nitrogen or oxygen atoms have not been found. Only those of the pyrrolidinium ions and pyrrolidine molecule have been introduced at calculated positions.

TABLE I Crystal data and structure refinement details

	1	**2**	**3**
Empirical formula	$C_{93}H_{133}N_{10}O_8$	$C_{89}H_{135}N_5O_{17}U_2$	$C_{97}H_{161}N_7O_{14}U_2$
$M/\mathrm{g\,mol^{-1}}$	1519.09	2023.08	2125.39
T/K	100(2)	100(2)	100(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	12.9415(6)	16.5768(14)	18.9255(9)
b/Å	18.4314(17)	16.6743(15)	24.9892(12)
c/Å	20.1309(18)	18.835(2)	22.6204(7)
$\alpha/°$	85.983(3)	95.616(5)	90
$\beta/°$	76.103(5)	101.992(6)	105.197(5)
$\gamma/°$	78.119(5)	115.792(5)	90
$V/\mathrm{Å}^3$	4560.3(6)	4479.1(7)	10323.8(8)
Z	2	2	4
μ/mm^{-1}	0.071	3.677	3.193
Reflections collected	25979	30840	66093
Independent reflections	15246	16990	18819
Observed reflections $[I > 2\sigma(I)]$	6741	8537	7273
R_{int}	0.107	0.107	0.077
Parameters refined	1061	1025	1101
R_1	0.114	0.118	0.097
wR_2	0.280	0.263	0.198

The pyrrolidine molecule corresponds either to N1 or N2, since di-protonation of both would result in a too short H···H contact. It has been assumed that N1 was di-protonated and N2 neutral.

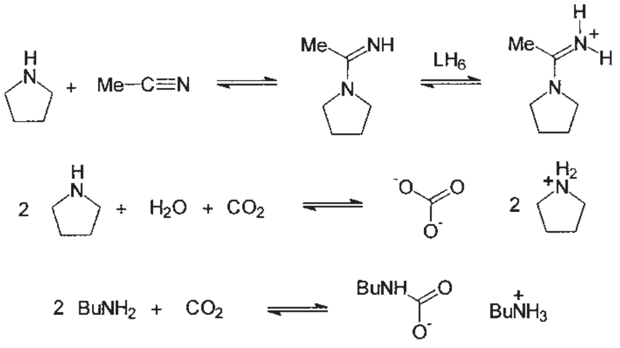
Compound **3**: All non-hydrogen atoms were refined with anisotropic displacement parameters. Some constraints on bond lengths and displacement parameters have been applied in *N*-butylcarbamate, butylammonium ions and butylamine molecules. The protons bound to nitrogen or oxygen atoms have not been found, nor introduced since their position cannot be calculated with certainty.

All the carbon-bound hydrogen atoms were introduced at calculated positions, except in the disordered parts. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (OH, NH, CH, CH_2) or 1.5 (CH_3) times that of the parent atom. Crystal data and refinement details are reported in Table I. The molecular plots were drawn with SHELXTL [17]. All calculations were performed on a Silicon Graphics R5000 workstation.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 183136–183138. 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

The determination of the crystal structures of the three compounds $[\mathrm{pyrC(CH_3)NH_2}]_2[\mathrm{LH_4}]\cdot 0.5\mathrm{pyrC(CH_3)NH}\cdot 5\mathrm{CH_3CN}$ **1** (pyr = pyrrolidine; $\mathrm{pyrC(CH_3)NH}$ = *N*,*N*-tetramethyleneacetamidine), $[\mathrm{Hpyr}]_4[(\mathrm{UO_2})_2\mathrm{L}(\mathrm{CO_3})]\cdot\mathrm{pyr}\cdot 2\mathrm{H_2O}$ **2** and $[\mathrm{BuNH_3}]_3[(\mathrm{UO_2})_2\mathrm{L}(\mathrm{BuNHCOO})]\cdot 3\mathrm{BuNH_2}$ **3** was rendered difficult by the low crystal quality and by the presence of unexpected molecules or ions resulting from spurious base/medium reactions. Such a reaction has previously been observed to take place between the tertiary amine DABCO (1,4-diazabicyclo[2.2.2] octane) and methylene chloride [4]. In the present cases, the bases used were either the primary butylamine or the secondary pyrrolidine. Both have been used in previous studies without any unexpected reaction being observed [5,6]. However, in the present cases, such reactions occurred along the reaction paths represented in Scheme 2. Pyrrolidine reacted with acetonitrile to form *N*,*N*-tetramethyleneacetamidine in compound **1**. In general, the formation of substituted amidines from primary or secondary amines and unactivated nitriles is disfavoured but pyrrolidine has been reported to react with acetonitrile under special conditions, namely in the presence of lanthanide(III) ions [18] and during a Cu(I) complex formation for which the crystal structure has been described [19,20]. As reported in Scheme 2, in the case of complex **3**, butylamine apparently reacted with CO_2 absorbed from the atmosphere to form butylammonium *N*-butylcarbamate. The latter salt has been reported to form on adding CO_2 to the amine [21]. As to the formation of carbonate ions in **2**, in the lack of mechanistic information, the simple reaction between CO_2 and H_2O absorbed by the basic medium (pyrrolidine and possibly *N*,*N*-tetramethyleneacetamidine) is assumed to take place. Unfortunately, only in these three cases were single crystals obtained.



SCHEME 2 Proposed base/medium reactions.

The metal-free macrocycle was obtained in crystal form as a doubly deprotonated species $[pyrC(CH_3)NH_2]_2[LH_4]\cdot 0.5pyrC(CH_3)NH\cdot 5CH_3CN$ **1**. The repeat unit of the triclinic cell contains one LH_4 dianion, two protonated and half a neutral *N*,*N*-tetramethyleneacetamidine molecules and five acetonitrile molecules, several parts of the structure being affected by some disorder. As illustrated in Fig. 1, the macrocycle assumes a *cone*-like (in the sense that all oxygen atoms are on the same side of the molecule) but an extremely elongated conformation. Each tri-phenolic subunit is held by two intramolecular hydrogen bonds linking its two terminal phenolic oxygen atoms to the central phenoxide (Table II), and each is independent from the other one. The elongated shape, with two pseudo-symmetry planes perpendicular to the mean plane of the molecule, one containing the ether atoms O4 and O8 and the other the phenoxide atoms O2 and O6, is completely different from the more circular shape of the [3.1.3.1.1.1] isomer [3]. The O2···O6 distance in **1** is 11.062(5) Å, whereas the O1···O3 and O5···O7 distances are 3.618(6) and 3.525(5) Å, respectively, the separation between the ether atoms O4 and O8 being 5.506(6) Å. The internal cavity defined by the oxygen atoms is in this way about twice as long as it is large and is obviously suggesting a ditopic ligand with two identical sites. The C–O–C–C torsion angles defined by the ether bridges are all *anti* angles

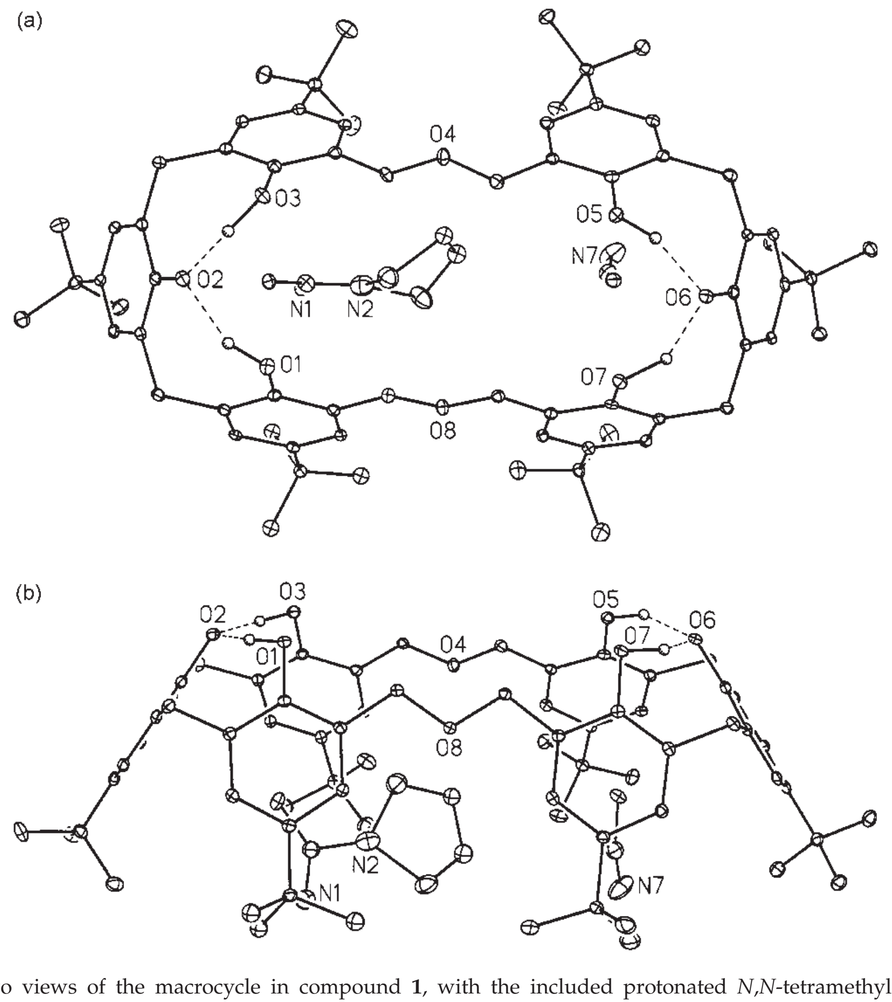
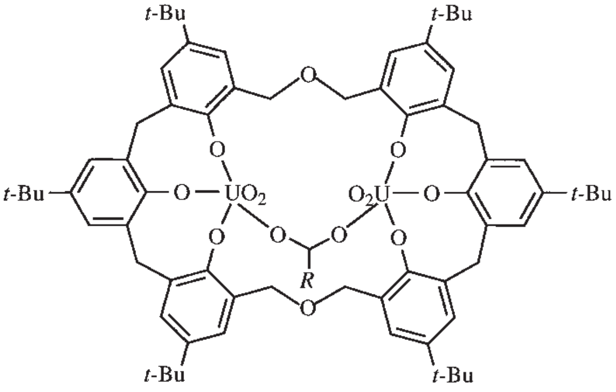


FIGURE 1 (a,b) Two views of the macrocycle in compound **1**, with the included protonated *N*,*N*-tetramethyleneacetamidine and acetonitrile molecules. Intramolecular hydrogen bonds are represented as dashed lines with hydrogen atoms as small spheres of arbitrary radii. Other hydrogen atoms, counter-ions and solvent molecules are omitted for clarity. Only one position of the disordered *tert*-butyl group and pyrrolidine ring are represented. Ellipsoids are drawn at the 10% probability level.

(173.6–177.9°), which results in a nearly planar "*w*" shape (if one considers the three atoms of the bridge and the two aromatic carbon atoms to which they are linked). The six phenol/phenoxide oxygen atoms define a plane with a rms deviation of 0.08 Å, with the ether atoms O4 and O8 at 1.408(5) and 1.595(5) Å from it. The reference plane comprising the four methylene links is nearly parallel to the O_6 mean plane, with a dihedral angle of 0.86(7)°. The dihedral angles between this plane and the aromatic rings are 60.0(1), 54.7(1), 61.4(1), 53.4(1), 58.3(1) and 63.0(1)°, indicating a rather deep internal cavity. One $pyrC(CH_3)NH_2$ cation and one acetonitrile molecule are included in this cavity, each roughly occupying a tri-phenolic subunit, which can be seen as a ditopic tendency of this macrocycle for inclusion in its cavity as well as for oxygen coordination. A second cation is located outside and is involved in a strong hydrogen bond with the phenoxide atom O6.

The two complexes $[Hpyr]_4[(UO_2)_2L(CO_3)]\cdot pyr\cdot 2H_2O$ **2** and $[BuNH_3]_3[(UO_2)_2L(BuNHCOO)]\cdot 3BuNH_2$ **3** (Scheme 3) present many common features and will be discussed together. These two complexes crystallize with one complex molecule in the repeat unit. In both of them, two uranyl ions are encompassed by the ligand, each of them in one of the two tri-phenolic subunits. Each uranyl ion is bound to three phenoxide oxygen atoms (Figs. 2 and 3), with U–O bond lengths in the range 2.17(2)–2.311(15) [mean value 2.25(4), including both compounds] Å, which is usual in poly-phenoxide calixarene complexes [1–7,9,10]. The square planar equatorial coordination, which is generally observed [1,2] is ensured by a bridging bidentate ion, CO_3^{2-} in **2** or $BuNHCOO^-$ in **3**. These ions are located close to the pseudo-symmetry plane containing the uranyl ions and bisecting the central aromatic rings of the tri-phenolic units, but the former has its uncomplexed oxygen atom directed towards the calixarene cavity whereas the latter has its aliphatic chain out of the cavity (Figs. 2b and 3b). The corresponding U–O bond lengths are in the range 2.306(12)–2.351(11) [mean value 2.32(2)]Å. A simpler explanation of the central bridge in compound **2** would have been to interpret it as an acetate ion; however, the bond length and the presence of a hydrogen bond involving the uncomplexed terminal atom do not support this view, but are in good agreement with the hypothesis of a carbonate ion. The four donor atoms around each uranyl ion define mean planes which contain the uranium atoms [deviations in the range 0.012(7)–0.079(6) Å]. The dihedral angles between these mean planes are 27.9(2) and 30.2(2)° in **2** and **3**, respectively. Each of the two tri-phenolic subunits is in the *cone* conformation, and the resulting macrocycles assume also *cone*-like conformations. If the mean plane defined by the four methylene links is taken as a reference plane (with rms deviations of 0.06 and 0.03 Å in **2** and **3**, respectively), the dihedral angles between the aromatic rings and this mean plane can be divided into two groups. The terminal rings of the tri-phenolic subunits correspond to dihedral angles in the range 57.2(5)–60.2(6)° in **2** and 54.9(5)–62.8(4)° in **3**, whereas the central rings correspond to dihedral angles of 69.0(5) and 73.4(5)° in **2** and 63.7(5) and 67.0(4)° in **3**. The central rings are thus more "vertical" than the terminal ones, and particularly so in compound **2**. Inside each compound, the two ether bridges present different conformations, which appears clearly if one considers the two C–O–C–C torsion angles defined by each bridge. The bridges containing O4 define two *anti* torsion angles (155.7–179.7°) and assume a nearly planar "*w*" shape as in compound **1**, whereas those around O8 define one *anti* and one *gauche* angle (80.2° in **2**, 69.0° in **3**) and, in this case, only three atoms out of the five defining the bridge are coplanar. The coexistence of bridges with these two different conformations has been encountered in several tetrahomodioxacalix[4]-arenes [22,23]. In both compounds, the presence of numerous counter-ions and solvent molecules results in the formation of intricated hydrogen bonding patterns. In compound **2**, one pyrrolidinium ion and a pyrrolidine molecule are located in the calixarene cavity and form hydrogen bonds one with the other and with the inwards-looking oxo groups of each uranyl ion and oxygen atom of the carbonate ion. Two other pyrrolidinium ions are located on the other side of the complex. One of them (N4) bridges two calixarene molecules, being hydrogen bonded to the phenoxide atom O1 and to atom O2 from a neighbouring molecule, while the other (N5) is hydrogen bonded to the coordinated carbonate atom O13. Other hydrogen bonds link the water molecules (O16 and O17), the ether oxygen atoms and the third pyrrolidinium ion. Two butylammonium ions are



2 *R* = O
3 *R* = NHBu

SCHEME 3 The anionic complex core in complexes **2** and **3**.

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

*Uranium environment in complexes **2** and **3***							
2	U1–O1	2.265(14)	U2–O5	2.31(2)			
	U1–O2	2.302(14)	U2–O6	2.218(14)			
	U1–O3	2.311(15)	U2–O7	2.17(2)			
	U1–O9	1.69(2)	U2–O11	1.791(13)			
	U1–O10	1.789(14)	U2–O12	1.67(2)			
	U1–O13	2.306(12)	U2–O14	2.31(2)			
	U1···U2	6.6875(12)					
	O1–U1–O2	87.5(5)	O5–U2–O6	83.8(5)			
	O2–U1–O3	83.6(5)	O6–U2–O7	86.4(5)			
	O1–U1–O13	93.3(5)	O5–U2–O14	95.0(5)			
	O3–U1–O13	96.1(5)	O7–U2–O14	94.9(5)			
	O9–U1–O10	177.8(6)	O11–U2–O12	177.6(6)			
3	U1–O1	2.234(11)	U2–O5	2.237(12)			
	U1–O2	2.223(11)	U2–O6	2.219(12)			
	U1–O3	2.254(11)	U2–O7	2.268(12)			
	U1–O9	1.744(12)	U2–O11	1.763(11)			
	U1–O10	1.761(11)	U2–O12	1.779(12)			
	U1–O13	2.351(11)	U2–O14	2.331(15)			
	U1···U2	6.5433(9)					
	O1–U1–O2	85.2(4)	O5–U2–O6	84.5(4)			
	O2–U1–O3	83.2(4)	O6–U2–O7	84.1(4)			
	O1–U1–O13	94.7(4)	O5–U2–O14	92.3(5)			
	O3–U1–O13	96.7(4)	O7–U2–O14	99.6(5)			
	O9–U1–O10	176.4(5)	O11–U2–O12	177.2(6)			
Hydrogen bonding geometry							
1							
O1···O2	2.595(5)	O1–H1	0.96	H1···O2	1.69	O1–H1···O2	157
O3···O2	2.474(5)	O3–H3	1.05	H3···O2	1.42	O3–H3···O2	180
O5···O6	2.564(5)	O5–H5	0.96	H5···O6	1.67	O5–H5···O6	152
O7···O6	2.571(5)	O7–H7	1.10	H7···O6	1.57	O7–H7···O6	148
N3···O6	2.765(6)	N3–H3A	0.86	H3A···O6	1.92	N3–H3A···O6	169
2							
N1···N2	2.74(3)	N1–H1A	0.90	H1A···N2	1.86	N1–H1A···N2	163
N1···O10	2.90(3)	N1–H1B	0.90	H1B···O10	2.10	N1–H1B···O10	148
N2···O12	2.89(2)	N2–H2	0.90	H2···O12	2.27	N2–H2···O12	127
N2···O15	2.70(3)	N2–H2	0.90	H2···O15	1.93	N2–H2···O15	142
N3···O16	2.81(3)	N3–H3A	0.90	H3A···O16	1.97	N3–H3A···O16	154
N3···O17′	2.78(3)	N3–H3B	0.90	H3B···O17	1.93	N3–H3B···O17	156
N4···O1	2.75(2)	N4–H4A	0.90	H4A···O1	1.87	N4–H4A···O1	166
N4···O2″	2.72(2)	N4–H4B	0.90	H4B···O2	1.82	N4–H4B···O2	174
N5···O13	2.82(4)	N5–H5A	0.90	H5A···O13	1.92	N5–H5A···O13	175
O16···O8*	2.77(2)	O17···O3*	2.64(2)				
3*							
N2···N7	2.72(4)	N2···O11	3.28(3)				
N2···O4	2.87(3)	N3···O1	2.78(3)				
N2···O10	3.09(3)	N4···O5	2.72(2)				

* Hydrogen atoms not found. *Symmetry codes*: $' = x, 1 + y, z$; $'' = -x, -y, 2 - z$

included in the calixarene cavity in compound **3**, one of them likely hydrogen bonded to oxo and ether oxygen atoms and the other to the first one only. The other counter-ions and amine molecules are located outside and hydrogen bonded between them and with phenoxide oxygen atoms; some of them are bridging two facing calixarenes through their phenoxide groups. Such arrangements are comparable to those which have been described and discussed in the case of primary and secondary amines and the uranyl ion complexes of hexahomotrioxacalix[3]arenes [5] and tetrahomodioxacalix[4]arenes [6]. The occurrence of cation–π interactions has been inferred from the short contacts present [5–7] and it will not be discussed further herein.

The structures of complexes **2** and **3**, when compared to that of the mononuclear uranyl complex of $L'H_6$, evidence the importance of the location of the ether links with respect to the six phenolic groups. As stated previously, LH_6 can obviously be considered as a ditopic ligand. The size of the two sites matches that of the uranyl ion and internal three-phenoxide coordination of the latter ensues. On the other hand, $L'H_6$ does not present two obvious coordinating sites. When in the presence of uranyl ions, it adopts a much distorted conformation, the cation being bound to the two phenoxide groups of the di-phenolic subunit and two other from the tetra-phenolic one and the uncomplexed part of the macrocycle is buckled away from

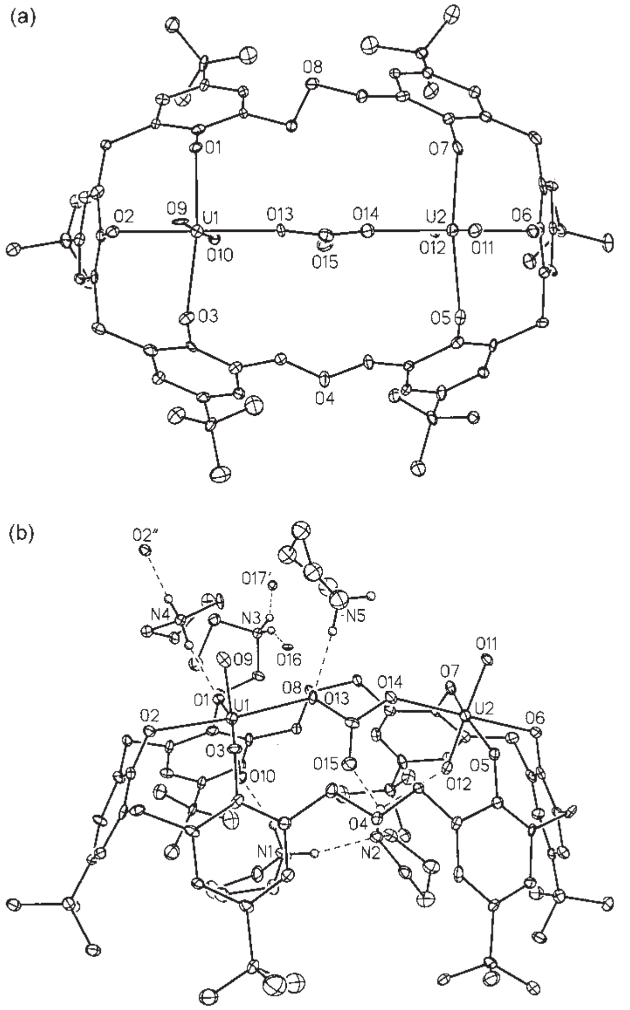


FIGURE 2 (a) View of the anionic complex molecule in compound **2**. Hydrogen atoms, counter-ions and solvent molecules are omitted for clarity. Ellipsoids are drawn at the 10% probability level. (b) View of complex **2** including counter-ions and solvent molecules. Hydrogen bonds are represented as dashed lines with hydrogen atoms as small spheres of arbitrary radii. Other hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 10% probability level. Symmetry codes: $' = x,\ 1 + y,\ z$; $'' = -x,\ -y,\ 2 - z$.

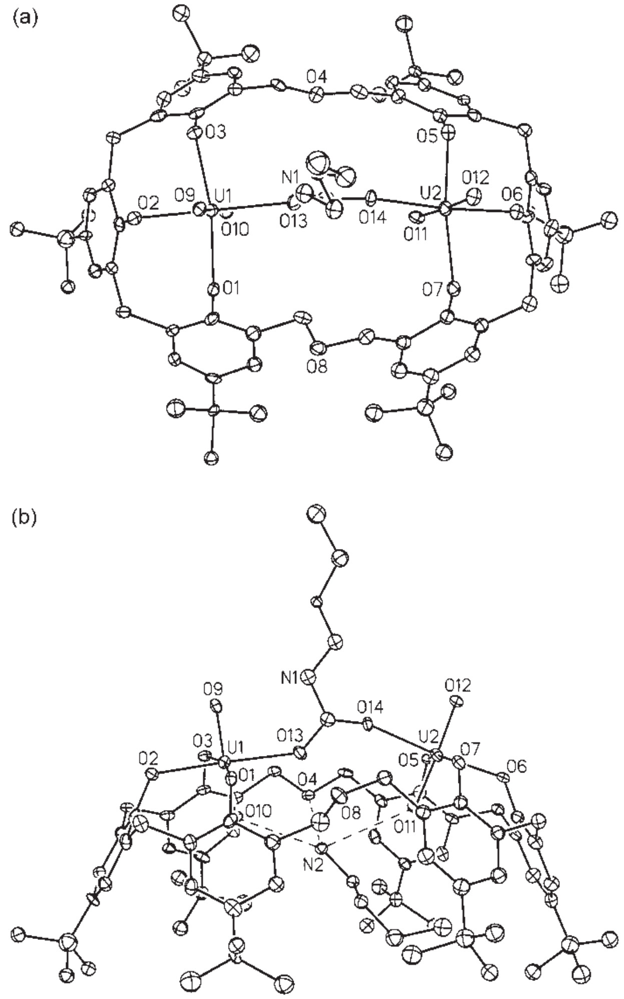


FIGURE 3 (a) View of the anionic complex molecule in compound **3**. Hydrogen atoms, counter-ions and solvent molecules are omitted for clarity. Ellipsoids are drawn at the 10% probability level. (b) View of complex **3** with the included and hydrogen bonded counter-ion. Possible hydrogen bonds are represented as dashed lines. Other counter-ions, solvent molecules and hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 10% probability level.

the complex core [3]. In the case of homooxacalixarenes, the prediction of the nuclearity of the complexes from the macrocycle size must of course be balanced by the more or less convenient location of the ether groups among positional isomers.

As indicated above, the size of LH_6 is intermediate between those of calix[7]arene and calix[8]arene (see Table III in Ref. [3]). It has the same number of bonds defining the central ring as calix[7]arene and a smaller one than calix[8]arene, but, when one considers the sum of the number of phenolic and ether groups, it is equal for LH_6 and calix[8]arene and smaller for calix[7]arene. *p-tert*-Butylcalix[8]arene complexes two uranyl ions, each of them bound to four oxygen atoms (two phenols and two phenoxides), and bridged by a central hydroxide ion [1,2,24,25], whereas *R*-calix[7]arene (*R* = *tert*-butyl, benzyl) complexes either one uranyl ion in its tetraphenolic subunit [9], either two uranyl ions with a U═O–U bond between them [10]. The direct bond between the two uranyl ions in the latter case can be attributed to a macrocycle size slightly too small for two independent cations. In the case of LH_6, both the size of the cavity and its shape permitted to expect a binuclear complex, which actually was observed. However, some interesting differences with the *p-tert*-butylcalix[8]arene complexes deserve mention. In **2** and **3**, the cations are in a square-planar equatorial environment, whereas they were in a pentagonal one in the *p-tert*-butylcalix[8]arene complexes, with one more coordinated phenolic oxygen atom. The U···U distance in the latter was about 4.5 Å, whereas it is much larger in the present cases (6.69 and 6.54 Å) as a result of the ligand elongated shape. As a consequence, a single bidentate hydroxide ion was acting as a bridge in the calix[8]arene complexes, which is replaced in **2** and **3** by a larger bidentate –COO species. It is also noteworthy that, in spite of the similarities between **2** and **3** and the calix[8]arene complexes, the conformations of the macrocycles are quite different, either in the free or in the complexed forms. *p-tert*-Butylcalix[8]arene adopts the so-called *pleated* or *undulated loop* conformation when it is free, with oxygen atoms alternately above and below the molecule mean plane [26,27] and a somewhat different, but rather flat conformation when complexed to uranyl ions, with groups of two oxygen atoms alternately above and below the molecule mean plane. On the other hand, LH_6, either metal-free and doubly deprotonated or complexed as a hexa-anion, assumes *cone*-like conformations and defines a rather deep cavity.

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