C(32)	0.832 (1)	0.4029 (8)	0.6466 (5)	4.8 (2)
C(33)	0.807 (1)	0.389 (1)	0.6999 (5)	8.2 (4)
C(34)	0.955 (1)	0.442 (1)	0.6296 (6)	8.6 (4)

Table 2. *Selected geometric parameters* (Å, °)

La···La^{i}	4.268 (2)	O(21)—C(21)	1.254 (4)
La···La^{ii}	5.524 (1)	O(22)—C(21^{ii})	1.232 (4)
La—OW(1)	2.590 (7)	O(31)—C(31)	1.253 (4)
La—OW(2)	2.551 (2)	O(32)—C(31)	1.259 (12)
La—O(11)	2.547 (5)	C(11)—C(12)	1.506 (4)
La—O(11^{i})	2.674 (5)	C(12)—C(13)	1.334 (6)
La—O(12)	2.601 (2)	C(12)—C(14)	1.446 (5)
La—O(21)	2.403 (2)	C(21)—C(22)	1.506 (5)
La—O(22)	2.462 (7)	C(22)—C(23)	1.371 (6)
La—O(31)	2.575 (2)	C(22)—C(24)	1.430 (6)
La—O(32)	2.672 (6)	C(31)—C(32)	1.504 (5)
O(11)—C(11)	1.283 (10)	C(32)—C(33)	1.333 (7)
O(12)—C(11^{i})	1.248 (4)	C(32)—C(34)	1.442 (7)
La^{ii}···La···La^{i}	122.37 (1)	O(11)—La—O(21)	102.57 (9)
OW(1)—La—OW(2)	138.50 (8)	O(11)—La—O(22)	136.74 (9)
OW(1)—La—O(11)	68.05 (8)	O(11)—La—O(31)	77.45 (8)
OW(1)—La—O(11^{i})	79.55 (8)	O(11)—La—O(32)	72.47 (8)
OW(1)—La—O(12)	119.65 (9)	O(11^{i})—La—O(12)	49.11 (7)
OW(1)—La—O(21)	72.89 (9)	O(11^{i})—La—O(21)	152.09 (8)
OW(1)—La—O(22)	73.59 (9)	O(11^{i})—La—O(22)	84.2 (2)
OW(1)—La—O(31)	125.8 (1)	O(11^{i})—La—O(31)	125.9 (2)
OW(1)—La—O(32)	139.64 (8)	O(11^{i})—La—O(32)	79.68 (8)
OW(2)—La—O(11)	147.64 (8)	O(12)—La—O(22)	71.99 (9)
OW(2)—La—O(11^{i})	123.8 (2)	O(12)—La—O(31)	110.99 (8)
OW(2)—La—O(12)	74.6 (2)	O(12)—La—O(32)	67.58 (8)
OW(2)—La—O(21)	77.2 (2)	O(21)—La—O(22)	84.1 (1)
OW(2)—La—O(22)	75.6 (1)	O(21)—La—O(31)	75.60 (9)
OW(2)—La—O(31)	71.3 (2)	O(21)—La—O(32)	124.97 (9)
OW(2)—La—O(32)	81.44 (8)	O(22)—La—O(31)	144.0 (1)
O(11)—La—O(11^{i})	70.24 (8)	O(22)—La—O(32)	137.40 (9)
O(11)—La—O(12)	110.80 (8)	O(31)—La—O(32)	49.52 (8)
O(12)—La—O(21)	146.64 (9)		

D—H···*A*	*D*···*A*	*D*—H···*A*
OW(1)—HW(11)···O(32^{i})	2.735 (3)	149.7 (2)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

Data collection was performed using *CAD*-4 *Software* (Enraf–Nonius, 1989). All non-H atoms were located by Patterson and Fourier techniques and refined by full-matrix least-squares methods with anisotropic displacement parameters. Most H atoms were located by the same methods and the remainder were placed in calculated positions. All H atoms were assigned a B_{iso} of 4.0 Å^2 and their parameters were not refined. All calculations were performed using *SDP* (Frenz, 1985), on a VAX II computer.

This work was supported by the Education Committee of Zhejiang province.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data, together with three packing diagrams, have been deposited with the IUCr (Reference: MU1143). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Deacon, G. B. & Phillips, R. J. (1980). *Coord. Chem. Rev.* **33**, 227–230.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Frenz, B. A. (1985). *SDP Structure Determination Package*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Hansson, E. (1975). *Acta Chem. Scand. Ser. A*, **29**, 927–934.
Ma, J.-F., Jin, Z.-S. & Ni, J.-Z. (1993). *Huaxue Xuebao*, **51**, 784–790. (In Chinese.)
Ma, A.-Z., Li, L.-M., Lin, Y.-H. & Xi, S.-Q. (1993). *Acta Cryst.* C**49**, 865–867.
Xue, W.-M., Zhu, Y. & Yang, R.-D. (1992). *J. Coord. Chem.* **26**, 199–204.

Acta Cryst. (1995). C**51**, 1570–1574

A Bimetallic Complex Between Uranyl and *p-tert*-Butylcalix[8]arene

Pierre Thuéry, Nelly Keller, Monique Lance,
Julien-Daniel Vigner and Martine Nierlich

*CEA, DSM/DRECAM/SCM, CE Saclay, Bâtiment 125,
91191 Gif-sur-Yvette, France*

(*Received* 25 *October* 1994; *accepted* 13 *January* 1995)

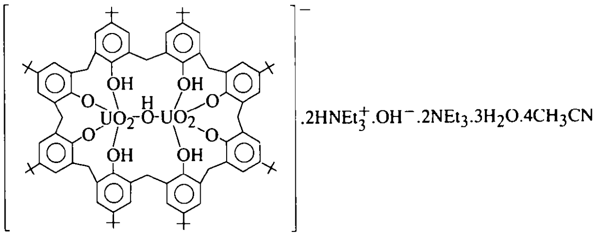
Abstract

$UO_2(NO_3)_2$ reacts with *p-tert*-butylcalix[8]arene, deprotonated with triethylamine as base, in acetonitrile to give the bimetallic complex μ-hydroxo-1:2κ^2O-μ-[5,11,17,23,29,35,41,47-octa-*tert*-butylnonacyclo[43.3.1.1^{3,7}.1^{9,13}.1^{15,19}.1^{21,25}.1^{27,31}.1^{33,37}.1^{39,43}]hexapentaconta-1(49),3,5,7(56),9,11,13(55),15,17,19(54),-21,23,25(53),27,29,31(52),33,35,37(51),39,41,43(50),-45,47-tetracosaene-49,50,51,52,53,54,55,56-octolato-1$\kappa^4O^{49,50,51,52}$:2$\kappa^4O^{53,54,55,56}$]bis[dioxouranium(VI)] with bis(triethylammonium) hydroxide bis(triethylamine) trihydrate tetraacetonitrile solvate, $(C_6H_{16}N)_2[(UO_2)_2(C_{88}H_{108}O_8)(OH)](OH).2C_6H_{15}N.3H_2O.4C_2H_3N$. The two uranyl ions are included in the fourfold deprotonated macrocycle, each of them being bonded to four phenolic O atoms, with a bridging hydroxyl ion ensuring the five-coordinate equatorial environment usual for a uranyl ion. A protonated triethylamine molecule is hydrogen bonded to one O atom of each uranyl moiety.

Comment

The ability of calixarenes to complex metallic cations has been the subject of extensive research in recent years (for reviews see: Gutsche, 1989; Bünzli & Harrowfield, 1991). Among large-metal-ion complexes, those containing lanthanides have been investigated particularly, both structurally and spectroscopically, while structurally characterized actinide complexes remain scarce, being limited to the complex of uranyl with bis(homooxa)-*p-tert*-butylcalix[4]arene (Harrowfield, Ogden & White, 1991*a*) and the bimetallic complex of thorium(IV) with *p-tert*-butylcalix[8]arene

(Harrowfield, Ogden & White, 1991*b*). However, it has been shown that water-soluble modified calixarenes called 'uranophiles' can achieve selective extraction of uranyl from sea water (Shinkai, 1991) and, in particular, that *p*-sulfonatocalix[8]arene is able to complex UO_2^{2+} in a 2:1 metal–ligand stoichiometry (Nagasaki, Kawano, Araki & Shinkai, 1991), but no structural information relative to the ion-binding mode is available in these cases. Recently, molecular-dynamics simulations have suggested the possibility of including the uranyl ion in [*p*-methylcalix[6]arene-6H] (with coordination to only five phenolato groups) and in [*p*-methylcalix[5]-arene-5H] (Guilbaud & Wipff, 1993). We report here the structure of a bimetallic complex between uranyl and *p*-*tert*-butylcalix[8]arene, (I). Some binuclear uranyl complexes with compartmental Schiff bases have already been described (Casellato, Guerriero, Tamburini, Vigato & Graziani, 1990); however, the complex reported here is, to our knowledge, the first bimetallic inclusion complex of uranyl in a macrocycle.



(I)

The structure determination gives the overall formula as $2HNEt_3^+.OH^-.[(UO_2^{2+})_2(H_4L^{4-})(OH^-)]^-.2NEt_3.3H_2O.4CH_3CN$ (where L^{8-} is the octaanion of *p*-*tert*-butylcalix[8]arene). *ORTEP*II (Johnson, 1976) drawings of the complex molecule are represented in Figs. 1 and 2. The asymmetric unit contains one half of the anionic complex molecule corresponding to the formula $[(UO_2^{2+})_2(H_4L^{4-})(OH^-)]^-$, the hydroxyl ion being located on the twofold crystallographic axis. The complex possesses two pseudo-mirror planes intersecting on the twofold axis, perpendicular to each other and to the mean plane of the molecule, one containing U, U^i and O(5), the other bisecting the line joining U and U^i [symmetry code: (i) $-x$, y, $\frac{1}{2}-z$]. Two UO_2^{2+} ions are encompassed by the macrocycle, each of them bonded in its equatorial plane to four phenolic O atoms (two of which are deprotonated) and one bridging OH^- anion, so as to produce the equatorial pseudo-planar pentacoordinate environment usual for the uranyl ion. The five O atoms surrounding the metal ion are coplanar with a maximum deviation of ±0.12 (1) Å, the U atom lying 0.010 (1) Å from this mean plane. The two mean planes, corresponding to the U and U^i environments, that share the hydroxyl O(5), make a dihedral angle of 146.1 (1)°. The U atoms are heptacoordinated, with a usual distorted pentagonal bipyramidal geometry and the linear uranyl moieties assuming normal geometric features. The four phenolic O atoms of the asymmetric unit divide into two groups of two atoms each, the first consisting of deprotonated O atoms [U—O(2) 2.218 (9) and U—O(3) 2.20 (1) Å] and the second of neutral phenolic O atoms [U—O(1) 2.619 (9) and U—O(4) 2.476 (9) Å], with a difference in U—O distances of about 0.3–0.4 Å between the two groups. The $U—O^-$ distances are comparable to those found in the complexes of the uranyl ion with Schiff bases (2.23 Å; Casellato *et al.*, 1990) and with bis(homooxa)-*p*-*tert*-butylcalix[4]arene (2.24–2.27 Å; Harrowfield *et al.*, 1991*a*). The mode of binding appears different to that already found in other homobimetallic *p*-*tert*-butylcalix[8]arene complexes, *i.e.* with Ti^{IV} isopropoxide (Hofmeister, Hahn & Pedersen, 1989) and Ln^{III} (Furphy, Harrowfield, Kepert, Skelton, White & Wilner, 1987; Harrowfield, Ogden, White & Wilner, 1989; Harrowfield, Ogden & White, 1991*c*,*d*), since none of the macrocyclic O atoms are bridging. However, there are some similarities with the binding mode observed in one of the two ligands of the Th^{IV} complex (Harrowfield, Ogden & White, 1991*b*), in which, as in our case, the two metal ions included in the cavity of the macrocycle are bonded to four phenolic O atoms and bridged by a hydroxyl ion.

A protonated triethylamine molecule [N(1)Et$_3$] is connected by a strong hydrogen bond to one of the uranyl O

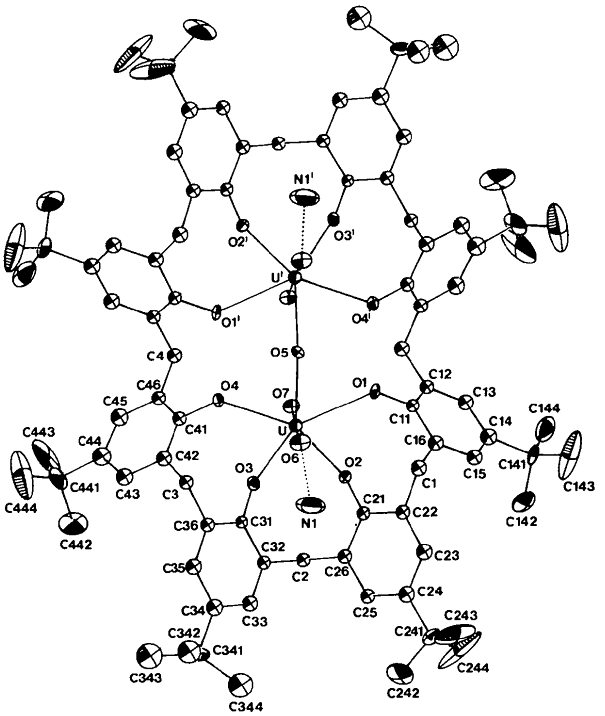


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the anionic complex molecule parallel to the mean plane [hydrogen bonds are shown as dashed lines; symmetry code: (i) $-x$, y, $\frac{1}{2}-z$]. Displacement ellipsoids are shown at the 40% probability level.

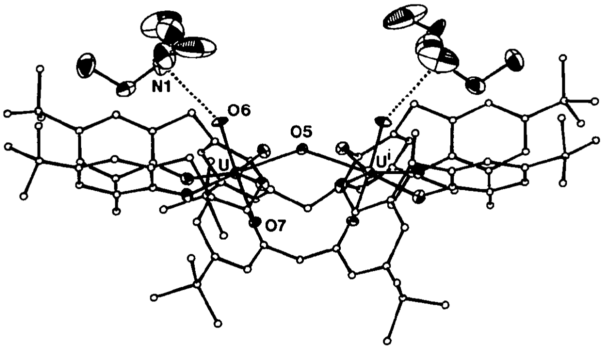


Fig. 2. *ORTEPII* (Johnson, 1976) drawing of the complex molecule, including the protonated triethylamine molecules (hydrogen bonds are shown as dashed lines). Displacement ellipsoids are shown at the 40% probability level. For clarity, the C atoms of the calixarene moiety are drawn as small spheres of arbitrary radii.

atoms. The N(1)···O(6) distance of 2.88 (3) Å is comparable to the shortest of previously published U—O···N distances (Franczyk, Czerwinski & Raymond, 1992), which range from 2.74 to 3.17 Å. Another triethylamine molecule is present which does not interact directly with the anionic complex molecule, but is instead involved in a hydrogen-bonding network with two water molecules [N(2)···O(8) 2.50 (3) and O(8)···O(9) 2.83 (3) Å]. The remaining positive charge is compensated for by a second hydroxyl ion [O(10)] located on the twofold axis and not involved in any hydrogen bonding.

The conformation of the calixarene can be described using the symbolic representation proposed recently by Ugozzoli & Andreetti (1992) as $C_2(+-,-+)_4$, where C_2 is the Schoenflies symbol for the point symmetry of the molecule and the + and − signs describe the sequence of signs of the φ and χ torsion angles around the macrocycle (given in Table 2). This conformation is identical to the one, described as a 'pleated loop', observed for the free calixarene in the solid state (Gutsche, Gutsche & Karaulov, 1985; Ugozzoli & Andreetti, 1992) and also in some mononuclear complexes (Harrowfield, Ogden, Richmond & White, 1991), but different from the 'propeller-like' or 'crown' conformations of the bimetallic complexes already described (Hofmeister *et al.*, 1989; Furphy *et al.*, 1987; Harrowfield *et al.*, 1989, 1991*c*,*d*). The configuration of the macrocycle may be determined, not only by the nature and preferred environment of the complexed metal ion, but also by the number of deprotonated phenolic O atoms. The twofold deprotonated form in the Eu^{3+} and Ca^{2+} mononuclear complexes, as well as the fourfold deprotonated form described here, are more similar to the neutral macrocycle than the six- or sevenfold deprotonated forms involved in the other bimetallic complexes cited previously. The cavity of the *p-tert*-butylcalix[8]arene thus appears particularly well suited to the inclusion of uranyl ions without any great distortion of conformation of the free macrocycle. In this case, the 'hole-size' matching plays a more important role than the high flexibility of the calixarene.

Experimental

The reaction between *p-tert*-butylcalix[8]arene and an excess of triethylamine in acetonitrile at room temperature, followed by the addition of two equivalents of uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, provides red–brown crystals of the title complex suitable for X-ray crystallography. The same reaction occurs when uranyl bis(trifluoromethanesulfonate), $UO_2(CF_3SO_3)_2$, is used in place of uranyl nitrate, and yields the same crystalline species.

Crystal data

$(C_6H_{16}N)_2[(UO_2)_2(C_{88}H_{108}O_8)(OH)](OH).2C_6H_{15}N.3H_2O.4C_2H_3N$
$M_r = 2493$
Monoclinic
$C2/c$
$a = 34.342\ (9)$ Å
$b = 12.642\ (2)$ Å
$c = 34.230\ (9)$ Å
$\beta = 119.43\ (2)°$
$V = 12943\ (6)$ Å^3
$Z = 4$
$D_x = 1.28$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8–12°$
$\mu = 2.43$ mm^{-1}
$T = 295$ K
Platelet
0.50 × 0.45 × 0.20 mm
Red–brown

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
6160 measured reflections
6026 independent reflections
3942 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.022$
$\theta_{\rm max} = 20°$
$h = 0 \rightarrow 33$
$k = 0 \rightarrow 12$
$l = -33 \rightarrow 33$
3 standard reflections frequency: 60 min intensity decay: insignificant

Refinement

Refinement on F
$R = 0.052$
$wR = 0.073$
$S = 2.92$
3942 reflections
459 parameters
H atoms not included
Unit weights applied

$(\Delta/\sigma)_{\rm max} = 0.04$
$\Delta\rho_{\rm max} = 1.03$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm iso}/B_{\rm eq}$
U	0.06627 (2)	0.12420 (6)	0.31278 (2)	2.69 (1)
O(6)	0.0817 (4)	−0.0156 (9)	0.3261 (4)	4.5 (4)
O(7)	0.0480 (3)	0.2596 (8)	0.2969 (3)	3.2 (3)
O(1)	−0.0016 (3)	0.1062 (9)	0.3271 (3)	3.0 (3)
O(2)	0.0888 (3)	0.1547 (8)	0.3846 (3)	2.9 (3)

O(3)	0.1370 (3)	0.1658 (9)	0.3390 (3)	3.0 (3)
O(4)	0.0789 (3)	0.1120 (9)	0.2477 (3)	3.1 (3)
O(5)	0	0.059 (1)	1/4	2.6 (4)
C(1)	0.0494 (5)	0.010 (2)	0.4152 (5)	4.0 (4)*
C(2)	0.1806 (5)	0.223 (1)	0.4323 (4)	2.8 (4)*
C(3)	0.1691 (5)	0.029 (1)	0.2973 (5)	3.1 (4)*
C(4)	0.0552 (5)	0.293 (1)	0.1899 (5)	3.7 (4)*
C(11)	−0.0062 (5)	0.153 (1)	0.3620 (4)	2.7 (4)*
C(12)	−0.0315 (5)	0.239 (1)	0.3559 (5)	3.0 (4)*
C(13)	−0.0363 (5)	0.280 (2)	0.3918 (5)	3.7 (4)*
C(14)	−0.0151 (5)	0.234 (2)	0.4320 (5)	4.2 (4)*
C(15)	0.0116 (5)	0.147 (1)	0.4399 (5)	3.7 (4)*
C(16)	0.0176 (5)	0.103 (1)	0.4056 (5)	3.6 (4)*
C(21)	0.1136 (4)	0.121 (1)	0.4251 (4)	2.7 (3)*
C(22)	0.0957 (5)	0.046 (1)	0.4440 (5)	3.0 (4)*
C(23)	0.1214 (5)	0.010 (2)	0.4877 (5)	3.8 (4)*
C(24)	0.1664 (5)	0.043 (2)	0.5141 (5)	4.2 (4)*
C(25)	0.1847 (5)	0.114 (1)	0.4957 (5)	3.4 (4)*
C(26)	0.1595 (5)	0.151 (1)	0.4508 (4)	2.9 (4)*
C(31)	0.1779 (4)	0.132 (1)	0.3648 (4)	2.3 (3)*
C(32)	0.2025 (5)	0.158 (1)	0.4108 (5)	2.8 (4)*
C(33)	0.2460 (5)	0.121 (2)	0.4366 (5)	3.5 (4)*
C(34)	0.2669 (6)	0.058 (2)	0.4188 (5)	4.3 (4)*
C(35)	0.2410 (5)	0.029 (2)	0.3730 (5)	4.0 (4)*
C(36)	0.1969 (5)	0.064 (1)	0.3462 (5)	2.9 (4)*
C(41)	0.1131 (5)	0.162 (1)	0.2434 (5)	3.0 (4)*
C(42)	0.1564 (5)	0.118 (1)	0.2670 (5)	3.5 (4)*
C(43)	0.1898 (6)	0.171 (2)	0.2618 (6)	4.6 (5)*
C(44)	0.1806 (6)	0.265 (2)	0.2344 (6)	5.4 (5)*
C(45)	0.1369 (6)	0.301 (2)	0.2120 (6)	4.8 (5)*
C(46)	0.1019 (5)	0.251 (1)	0.2163 (5)	3.0 (4)*
C(141)	−0.0207 (6)	0.277 (2)	0.4730 (5)	7.0 (7)
C(142)	0.0258 (9)	0.317 (3)	0.5091 (8)	13 (1)
C(143)	−0.0374 (8)	0.188 (3)	0.4909 (7)	17.9 (9)
C(144)	−0.0499 (9)	0.373 (3)	0.4604 (7)	13 (1)
C(241)	0.1939 (6)	0.010 (2)	0.5636 (6)	6.4 (7)
C(242)	0.242 (1)	−0.006 (4)	0.577 (1)	13 (2)
C(243)	0.192 (1)	0.088 (4)	0.593 (1)	18 (2)
C(244)	0.183 (1)	−0.096 (3)	0.5718 (9)	20 (2)
C(341)	0.3177 (6)	0.022 (2)	0.4478 (6)	7.7 (7)
C(342)	0.321 (1)	−0.093 (3)	0.438 (1)	11 (1)*
C(343)	0.340 (1)	0.061 (4)	0.420 (1)	10 (1)*
C(344)	0.326 (1)	0.000 (3)	0.498 (1)	11 (1)*
C(345)	0.344 (2)	0.095 (5)	0.484 (2)	11 (2)*
C(441)	0.2194 (6)	0.324 (3)	0.2295 (8)	10.7 (9)
C(442)	0.253 (1)	0.362 (3)	0.277 (1)	12 (1)
C(443)	0.204 (1)	0.437 (4)	0.210 (1)	14 (2)
C(444)	0.235 (1)	0.255 (4)	0.204 (1)	17 (2)
N(1)	0.1372 (7)	−0.184 (2)	0.3822 (7)	10.5 (9)
C(101)	0.1067 (9)	−0.233 (3)	0.404 (1)	18 (2)
C(102)	0.070 (1)	−0.266 (3)	0.383 (2)	27 (2)
C(103)	0.1713 (8)	−0.114 (2)	0.4174 (7)	7.5 (8)
C(104)	0.2087 (9)	−0.181 (3)	0.4567 (8)	10 (1)
C(105)	0.151 (1)	−0.245 (3)	0.352 (1)	17 (2)
C(106)	0.180 (1)	−0.239 (3)	0.341 (1)	19 (1)
N(2)	0.0801 (7)	−0.184 (2)	0.1649 (7)	14.0 (8)
C(201)	0.0800 (9)	−0.078 (3)	0.1302 (8)	17 (1)
C(202)	0.1111 (8)	0.011 (3)	0.1501 (8)	16 (1)
C(203)	0.1252 (8)	−0.238 (2)	0.1860 (8)	12.6 (9)
C(204)	0.122 (1)	−0.327 (3)	0.143 (1)	21 (1)
C(205)	0.0403 (9)	−0.283 (2)	0.1407 (8)	16 (1)
C(206)	0.064 (2)	−0.400 (4)	0.155 (2)	22 (1)
O(8)	0.0617 (9)	−0.122 (2)	0.2232 (8)	20 (1)
O(9)	1/2	0.309 (3)	1/4	18 (1)
O(10)	0	0.497 (4)	1/4	22 (2)
N(3)	0.068	0.385	0.400	15.0*
C(301)	0.050	0.463	0.408	15.0*
C(302)	0.035	0.536	0.423	15.0*
N(4)	0.149	0.392	0.318	15.0*
C(401)	0.157	0.485	0.295	15.0*
C(402)	0.159	0.550	0.276	15.0*

* $B_{\rm iso}$

Table 2. *Selected geometric parameters* (Å, °)

U—O(6)	1.84 (1)	U—O(7)	1.81 (1)
U—O(1)	2.619 (9)	U—O(2)	2.218 (9)
U—O(3)	2.20 (1)	U—O(4)	2.476 (9)
U—O(5)	2.381 (5)		
O(1)—C(11)	1.41 (2)	O(2)—C(21)	1.29 (2)
O(3)—C(31)	1.31 (2)	O(4)—C(41)	1.40 (2)
C(1)—C(16)	1.53 (2)	C(1)—C(22)	1.47 (2)
C(2)—C(26)	1.49 (2)	C(2)—C(32)	1.52 (2)
C(3)—C(36)	1.53 (2)	C(3)—C(42)	1.45 (2)
C(4)—C(46)	1.50 (2)	C(4)—C(12^{i})	1.53 (2)
C(14)—C(141)	1.60 (2)	C(141)—C(142)	1.55 (3)
C(141)—C(143)	1.52 (4)	C(141)—C(144)	1.49 (4)
C(24)—C(241)	1.54 (3)	C(241)—C(242)	1.50 (4)
C(241)—C(243)	1.44 (4)	C(241)—C(244)	1.45 (4)
C(34)—C(341)	1.59 (2)	C(341)—C(342)	1.50 (4)
C(341)—C(343)	1.56 (4)	C(341)—C(344)	1.62 (4)
C(341)—C(345)	1.46 (6)	C(44)—C(441)	1.61 (3)
C(441)—C(442)	1.53 (4)	C(441)—C(443)	1.56 (5)
C(441)—C(444)	1.50 (5)		
N(1)—C(101)	1.67 (5)	N(1)—C(103)	1.50 (3)
N(1)—C(105)	1.54 (5)	C(101)—C(102)	1.18 (5)
C(103)—C(104)	1.58 (3)	C(105)—C(106)	1.23 (5)
N(2)—C(201)	1.79 (4)	N(2)—C(203)	1.51 (3)
N(2)—C(205)	1.73 (3)	C(201)—C(202)	1.47 (5)
C(203)—C(204)	1.82 (4)	C(205)—C(206)	1.64 (5)
O(6)—U—O(7)	176.7 (5)	O(6)—U—O(1)	92.6 (4)
O(6)—U—O(2)	89.5 (4)	O(6)—U—O(3)	90.1 (4)
O(6)—U—O(4)	90.4 (4)	O(6)—U—O(5)	85.6 (5)
O(7)—U—O(1)	85.9 (4)	O(7)—U—O(2)	92.8 (4)
O(7)—U—O(3)	92.7 (4)	O(7)—U—O(4)	88.7 (4)
O(7)—U—O(5)	91.1 (5)	O(1)—U—O(2)	70.5 (3)
O(2)—U—O(3)	78.0 (3)	O(3)—U—O(4)	74.7 (3)
O(4)—U—O(5)	71.3 (2)	O(5)—U—O(1)	66.1 (2)
C(16)—C(1)—C(22)	109 (1)	C(26)—C(2)—C(32)	110 (1)
C(36)—C(3)—C(42)	111 (1)	C(12^{i})—C(4)—C(46)	109 (1)
C(14)—C(141)—C(142)	107 (2)	C(14)—C(141)—C(143)	109 (2)
C(14)—C(141)—C(144)	112 (2)	C(142)—C(141)—C(143)	111 (3)
C(142)—C(141)—C(144)	104 (3)	C(143)—C(141)—C(144)	113 (3)
C(24)—C(241)—C(242)	111 (2)	C(24)—C(241)—C(243)	112 (3)
C(24)—C(241)—C(244)	113 (2)	C(242)—C(241)—C(243)	108 (3)
C(242)—C(241)—C(244)	99 (3)	C(243)—C(241)—C(244)	114 (3)
C(34)—C(341)—C(342)	109 (2)	C(34)—C(341)—C(343)	104 (2)
C(34)—C(341)—C(344)	107 (2)	C(34)—C(341)—C(345)	112 (3)
C(44)—C(441)—C(442)	105 (2)	C(44)—C(441)—C(443)	110 (3)
C(44)—C(441)—C(444)	110 (3)	C(442)—C(441)—C(443)	95 (4)
C(442)—C(441)—C(444)	120 (3)	C(443)—C(441)—C(444)	115 (3)
C(101)—N(1)—C(103)	106 (2)	C(101)—N(1)—C(105)	125 (3)
C(103)—N(1)—C(105)	118 (3)	N(1)—C(101)—C(102)	125 (6)
N(1)—C(103)—C(104)	111 (2)	N(1)—C(105)—C(106)	138 (5)
C(201)—N(2)—C(203)	109 (2)	C(201)—N(2)—C(205)	119 (2)
C(203)—N(2)—C(205)	106 (2)	N(2)—C(201)—C(202)	120 (3)
N(2)—C(203)—C(204)	105 (2)	N(2)—C(205)—C(206)	111 (3)

C(15)—C(16)—C(1)—C(22)	−68 (2)
C(16)—C(1)—C(22)—C(23)	113 (2)
C(25)—C(26)—C(2)—C(32)	90 (2)
C(26)—C(2)—C(32)—C(33)	−86 (2)
C(35)—C(36)—C(3)—C(42)	−118 (2)
C(36)—C(3)—C(42)—C(43)	70 (2)
C(45)—C(46)—C(4)—C(12^{i})	89 (2)
C(46)—C(4)—C(12^{i})—C(13^{i})	−85 (1)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

A Lorentz–polarization correction was applied. The U atoms were located from a Patterson map interpretation using *SHELXS*86 (Sheldrick, 1985), the remaining atoms being determined from subsequent Fourier differences. Refinement was by full-matrix least squares (*MolEN*; Fair, 1990) with anisotropic displacement parameters for the U and O atoms, the triethylamine moieties and the *tert*-butyl groups of the calixarene molecule (except that of cycle 3, which was modelled with four isotropic terminal C atoms). The acetonitrile molecules were found and held fixed in the final refinement cycles. All calculations were performed on a VAX 4200 computer.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: NA1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bünzli, J. C. G. & Harrowfield, J. M. (1991). *Calixarenes: A Versatile Class of Macrocyclic Compounds*, edited by J. Vicens & V. Böhmer, pp. 211–231. Dordrecht: Kluwer Academic Publishers.

Casellato, U., Guerriero, P., Tamburini, S., Vigato, P. A. & Graziani, R. (1990). *J. Chem. Soc. Dalton Trans.* pp. 1533–1541.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Franczyk, T. S., Czerwinski, K. R. & Raymond, K. N. (1992). *J. Am. Chem. Soc.* **114**, 8138–8146, and references therein.

Furphy, B. M., Harrowfield, J. M., Kepert, D. L., Skelton, B. W., White, A. H. & Wilner, F. R. (1987). *Inorg. Chem.* **26**, 4231–4236.

Guilbaud, P. & Wipff, G. (1993). *J. Incl. Phenom.* **16**, 169–188.

Gutsche, C. D. (1989). In *Calixarenes. Monographs in Supramolecular Chemistry*, edited by J. F. Stoddart. Cambridge: Royal Society of Chemistry.

Gutsche, C. D., Gutsche, A. E. & Karaulov, A. I. (1985). *J. Incl. Phenom.* **3**, 447–451.

Harrowfield, J. M., Ogden, M. I., Richmond, W. R. & White, A. H. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2153–2160.

Harrowfield, J. M., Ogden, M. I. & White, A. H. (1991*a*). *J. Chem. Soc. Dalton Trans.* pp. 979–985.

Harrowfield, J. M., Ogden, M. I. & White, A. H. (1991*b*). *J. Chem. Soc. Dalton Trans.* pp. 2625–2632.

Harrowfield, J. M., Ogden, M. I. & White, A. H. (1991*c*). *Aust. J. Chem.* **44**, 1237–1247.

Harrowfield, J. M., Ogden, M. I. & White, A. H. (1991*d*). *Aust. J. Chem.* **44**, 1249–1262.

Harrowfield, J. M., Ogden, M. I., White, A. H. & Wilner, F. R. (1989). *Aust. J. Chem.* **42**, 949–958.

Hofmeister, G. E., Hahn, F. E. & Pedersen, S. F. (1989). *J. Am. Chem. Soc.* **111**, 2318–2319.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Nagasaki, T., Kawano, K., Araki, K. & Shinkai, S. (1991). *J. Chem. Soc. Perkin Trans.* 2, pp. 1325–1327.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Shinkai, S. (1991). *Calixarenes: A Versatile Class of Macrocyclic Compounds*, edited by J. Vicens & V. Böhmer, pp. 173–198. Dordrecht: Kluwer Academic Publishers.

Ugozzoli, F. & Andreetti, G. D. (1992). *J. Incl. Phenom.* **13**, 337–348.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.