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Crystal Structure of a Uranyl/*p-tert*-Butylcalix[5]-arene Complex

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Abstract. The synthesis and crystal structure of the inclusion complex between uranyl and *p-tert*-butylcalix[5]arene are reported. $[UO_2(p\text{-}tert\text{-butylcalix[5]arene-4H})]^{2-} \cdot 2HNEt_3^+ \cdot 2MeOH$ (**1**) crystallizes in the monoclinic space group $C2/c$, $a = 30.06(2)$, $b = 18.20(3)$, $c = 31.35(2)$ Å, $\beta = 128.51(6)°$, $V = 13423(40)$ Å^3, $Z = 8$. Refinement led to a final conventional R value of 0.043 for 4155 reflections. The uranyl ion is bonded, in its equatorial plane, to the five oxygen atoms of the calixarene, four of which are deprotonated. A protonated triethylamine molecule is located inside the calixarene cavity and hydrogen bonded to a uranyl oxygen atom, and another one outside and hydrogen bonded to a calixarene oxygen atom. The calixarene conformation is the usual *cone* one.

1. Introduction

Few crystal structures of actinide complexes of calixarenes have been reported to date. The complexes described are the inclusion compounds of uranyl in bis(homo-oxa)-*p-tert*-butylcalix[4]arene [1] and *p-tert*-butylcalix[8]arene [2,3] and that of thorium in *p-tert*-butylcalix[8]arene [4], and also a dimeric species formed by uranyl and *p-tert*-butylcalix[6]arene, in which the two calixarene moieties are bridged by two uranyl ions [5]. The cavity size of bis(homo-oxa)-*p-tert*-butylcalix[4]arene appeared well suited for the inclusion of one uranyl ion bonded to the four phenolic oxygen atoms, whereas that of *p-tert*-butylcalix[8]arene is large enough to accommodate two uranyl or thorium ions. Some molecular modeling calculations have shown that the uranyl ion can be included in the cavity of *p-tert*-butylcalix[5]arene with bonding to the five oxygen atoms and in that of *p-tert*-butylcalix[6]arene with bonding to five out of the six oxygen atoms, with an upside-down reversal of the nonbonded phenolic unit with respect to the *pinched cone* conformation [6]. Many experimental solution studies have shown the complexing ability of various derivatives of calix[n]arenes (n = 5, 6 and 8) for uranyl ions [7]. Due to difficult chemical synthesis processes, few structures involving *p-tert*-butylcalix[5]arene or its derivatives have been reported so far [8–12]: we

report in this paper the synthesis and crystal structure of the uranyl complex of
p-tert-butylcalix[5]arene, with the aim of gaining insight about the complexing
mode of this ligand.

2. Experimental

2.1. SYNTHESIS

p-tert-Butylcalix[5]arene (0.3 mmol, purchased from Fluka and used without fur-
ther purification) was dissolved in 17 mL of chloroform and 7 mL of triethylamine.
The slow addition of a solution of 0.3 mmol of uranyl nitrate hexahydrate in 15 mL
of acetonitrile resulted in a deep red solution, which was evaporated to dryness.
Recrystallization from chloroform : methanol (1 : 1) yielded beautiful red crystals
suitable for X-ray crystallography.

2.2. CRYSTAL STRUCTURE ANALYSIS

2.2.1. *Crystal Data*

$[UO_2(\text{*p-tert*-butylcalix[5]arene}-4H)]^{2-} \cdot 2HNEt_3^+ \cdot 2MeOH$, $UO_9N_2C_{69}H_{106}$, formu-
la weight 1345.65; monoclinic, space group $C2/c$, $a = 30.06(2)$, $b = 18.20(3)$, $c = 31.35(2)$ Å, $\beta = 128.51(6)°$, $V = 13423(40)$ Å^3, $Z = 8$, $D_x = 1.332$, $\mu = 23.4 \text{ cm}^{-1}$.

2.2.2. *Measurements*

The diffraction experiment was performed with an Enraf-Nonius CAD4 diffrac-
tometer using MoK_α radiation. The crystal ($0.65 \times 0.55 \times 0.35 \text{ mm}^3$) was intro-
duced in a glass capillary. The lattice parameters were determined from the least-
squares refinement of the setting angles of 25 reflections ($8 < \theta < 12°$). The
data were collected in the range $1 < \theta < 20°$, in the ω/θ scan mode, at 295
K. The intensity decay was estimated from three standard reflections, measured
every 60 min (-1.6% in 68 h, linearly corrected). The data were corrected for
Lorentz-polarization effects, and for absorption effects with the ψ-scans method
[13] ($T_{\min} = 0.84$, $T_{\max} = 1.00$).

2.2.3. *Structure Analysis*

The structure was solved with SHELXS-86 [14] and refined by full-matrix least-
squares on F. Hydrogen atoms bonded to carbon atoms of the calixarene moiety
were located at their ideal positions (C—H 0.95 Å, B 6 Å^2) and constrained to
ride their parent carbon atom. Analytical scattering factors for neutral atoms [15]
were corrected for the anomalous dispersion terms $\Delta f'$ and $\Delta f''$. All calcula-
tions have been performed on a Vax 4000-200 computer, with the Enraf-Nonius
MolEN system [16]. 4155 observations with $I > 3\sigma(I)$, out of 6240 unique reflec-
tions measured, were used. Five hundred and nineteen parameters were refined
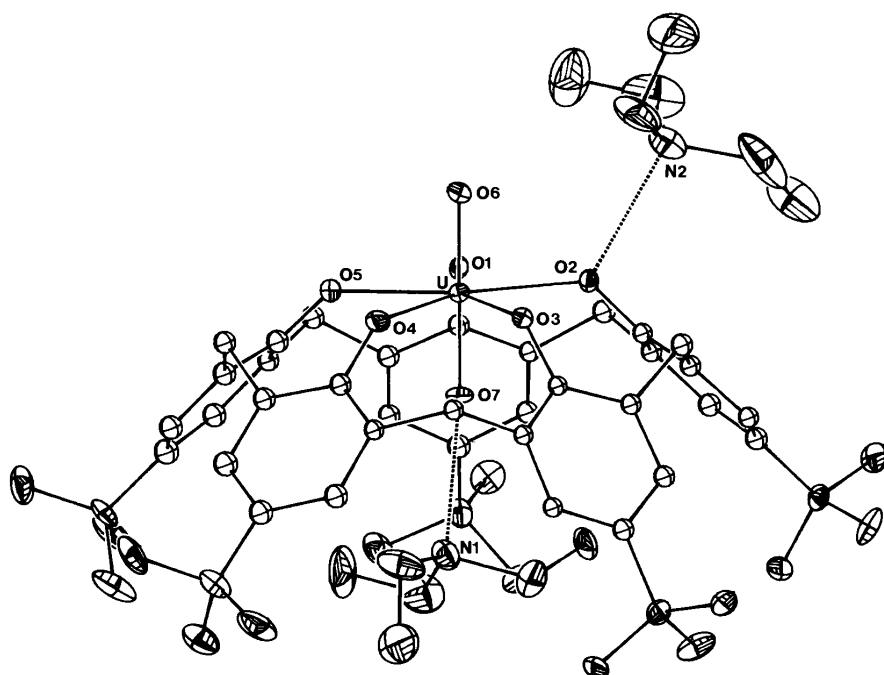
Figure 1. Molecular unit of (**1**). Solvent molecules omitted. Hydrogen bonds in dashed lines.

(anisotropic displacement parameters for uranium and oxygen atoms and for the *tert*-butyl groups and the triethylammonium ions; the solvent molecules were found in the last Fourier differences and fixed in the refinement). The final R values were $R = 0.043$ and $R_w = 0.053$ ($w = 1/\sigma(F)^2$) and the maximum residual density 0.73 e Å^{-3} (except for two peaks at 1.0–1.8 e Å^{-3} located at 1.0–1.3 Å from uranium and due to imperfect absorption corrections, as is often observed in uranium complexes; the imperfect geometry of the linear uranyl ion in this structure (O—U—O 176.1(3)°) may also arise from absorption effects [17]).

ORTEPII [18] drawings of the molecular unit of (**1**) are represented in Figures 1 and 2, fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table I and selected bond distances and angles in Table II.

3. Discussion of Results

The structure determination gives the overall formula $[(UO_2^{2+})(HL^{4-})]^{2-} \cdot 2HNEt_3^+ \cdot 2MeOH$, where L^{5-} is the pentaanion of *p-tert*-butycalix[5]arene. The complex molecule does not possess any symmetry element. The uranyl ion is located in the calixarene *lower-rim* cavity, and is bonded, in its equatorial plane, to the five oxygen atoms. However, the U—O distances are not all equivalent: three of them (with O(1), O(2) and O(5)) are in the range 2.25–2.30 Å, the fourth one (with O(3)) is longer (2.571(7) Å) and the fifth one (with O(4)) even longer (2.836(8) Å).

Table I. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters for non-hydrogen atoms, with ESD in parentheses. Starred atoms were refined anisotropically ($B_{\text{eq.}} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j$).

Atom	x/a	y/b	z/c	$B_{\text{iso.}}, B_{\text{eq.}}$
Complex molecule				
U	0.22740(1)	0.85521(2)	0.30126(1)	3.297(9)*
O(1)	0.1352(2)	0.8517(4)	0.2267(2)	3.4(2)*
O(2)	0.1801(2)	0.8919(4)	0.3337(2)	3.3(2)*
O(3)	0.3099(2)	0.8804(4)	0.4023(2)	3.5(2)*
O(4)	0.3440(2)	0.8330(4)	0.3517(2)	4.3(2)*
O(5)	0.2364(2)	0.8127(4)	0.2392(2)	3.7(2)*
O(6)	0.2248(2)	0.7637(4)	0.3198(2)	4.4(2)*
O(7)	0.2347(2)	0.9481(4)	0.2870(2)	3.9(2)*
C(1)	0.0712(3)	0.9489(6)	0.2410(3)	3.7(2)
C(2)	0.2531(3)	0.9651(6)	0.4339(3)	3.6(2)
C(3)	0.4251(3)	0.9201(6)	0.4439(3)	3.3(2)
C(4)	0.3437(4)	0.8087(6)	0.2629(3)	3.7(2)
C(5)	0.1339(3)	0.8555(6)	0.1352(3)	3.7(2)
C(11)	0.1092(3)	0.9086(6)	0.1922(3)	3.2(2)
C(12)	0.0786(3)	0.9604(6)	0.1989(3)	3.1(2)
C(13)	0.0543(4)	1.0193(6)	0.1638(4)	3.8(2)
C(14)	0.0567(3)	1.0320(6)	0.1214(3)	3.7(2)
C(15)	0.0842(4)	0.9751(6)	0.1146(4)	3.9(2)
C(16)	0.1093(3)	0.9158(6)	0.1477(3)	3.4(2)
C(17)	0.0279(4)	1.0982(7)	0.0834(4)	4.8(3)*
C(18)	−0.0363(4)	1.0881(7)	0.0492(4)	6.3(4)*
C(19)	0.0413(5)	1.1048(8)	0.0450(4)	8.5(5)*
C(20)	0.0459(5)	1.1688(7)	0.1155(4)	6.2(4)*
C(21)	0.1635(3)	0.9595(6)	0.3373(3)	3.0(2)
C(22)	0.1969(3)	0.9968(6)	0.3865(3)	3.0(2)
C(23)	0.1789(3)	1.0637(6)	0.3913(3)	3.1(2)
C(24)	0.1293(3)	1.0971(6)	0.3490(3)	3.2(2)
C(25)	0.0956(3)	1.0577(6)	0.3002(3)	3.6(2)
C(26)	0.1115(3)	0.9895(6)	0.2942(3)	3.1(2)
C(27)	0.1105(3)	1.1720(6)	0.3537(3)	3.7(3)*
C(28)	0.1052(4)	1.2254(7)	0.3139(4)	6.8(4)*
C(29)	0.0549(4)	1.1664(7)	0.3433(4)	7.3(4)*
C(30)	0.1524(5)	1.2044(8)	0.4112(4)	8.1(5)*
C(31)	0.3311(3)	0.9480(6)	0.4256(3)	2.8(2)
C(32)	0.3832(3)	0.9724(6)	0.4412(3)	2.8(2)
C(33)	0.3992(3)	1.0448(6)	0.4565(3)	3.3(2)
C(34)	0.3685(3)	1.0932(6)	0.4631(3)	3.0(2)
C(35)	0.3222(3)	1.0642(6)	0.4553(3)	3.6(2)
C(36)	0.3034(3)	0.9929(6)	0.4380(3)	2.9(2)
C(37)	0.3874(4)	1.1728(6)	0.4813(4)	4.0(3)*

Table I. Continued.

| Atom	x/a	y/b	z/c	$B_{\text{iso.}}, B_{\text{eq.}}$
Complex molecule				
C(38)	0.4149(4)	1.1794(7)	0.5413(4)	5.7(4)*
C(39)	0.3375(4)	1.2261(7)	0.4505(5)	7.5(5)*
C(40)	0.4300(4)	1.1975(7)	0.4741(4)	6.8(4)*
C(41)	0.3830(3)	0.8723(5)	0.3513(3)	3.1(2)
C(42)	0.3840(3)	0.8627(6)	0.3076(3)	3.6(2)
C(43)	0.4234(4)	0.9026(6)	0.3077(4)	4.4(3)
C(44)	0.4622(4)	0.9499(7)	0.3486(4)	4.3(3)
C(45)	0.4609(3)	0.9562(6)	0.3926(3)	3.9(2)
C(46)	0.4227(3)	0.9166(6)	0.3945(3)	3.1(2)
C(47)	0.5044(4)	0.9925(8)	0.3463(4)	5.7(4)*
C(48)	0.5473(5)	1.0335(9)	0.3964(5)	10.0(5)*
C(49)	0.4720(5)	1.0446(8)	0.2972(4)	8.4(5)*
C(50)	0.5356(4)	0.9371(9)	0.3346(4)	9.6(5)*
C(51)	0.2395(4)	0.8428(6)	0.2020(3)	3.7(2)
C(52)	0.1914(3)	0.8676(6)	0.1519(3)	3.2(2)
C(53)	0.1972(3)	0.9004(6)	0.1153(3)	3.7(2)
C(54)	0.2493(4)	0.9096(6)	0.1263(4)	4.1(3)
C(55)	0.2969(4)	0.8794(6)	0.1758(4)	4.0(3)
C(56)	0.2924(3)	0.8459(6)	0.2123(3)	3.8(2)
C(57)	0.2553(4)	0.9451(7)	0.0861(3)	4.6(3)*
C(58)	0.2025(5)	0.9800(9)	0.0389(5)	11.3(5)*
C(59)	0.2989(5)	1.0047(9)	0.1131(5)	10.9(6)*
C(60)	0.2780(5)	0.8927(9)	0.0675(4)	9.8(5)*
Triethylammonium ions				
N(1)	0.2637(3)	1.0826(6)	0.2706(3)	6.3(3)*
C(61)	0.3245(6)	1.070(1)	0.2978(6)	11.8(7)*
C(62)	0.3550(6)	1.134(1)	0.3050(7)	15.6(8)*
C(63)	0.2319(7)	1.116(1)	0.2206(5)	11.5(7)*
C(64)	0.2256(7)	1.080(1)	0.1778(5)	19.7(9)*
C(65)	0.2600(5)	1.1292(8)	0.3091(5)	10.1(5)*
C(66)	0.2101(4)	1.1295(9)	0.3016(4)	9.4(4)*
N(2)	0.1378(4)	0.7986(8)	0.3684(4)	8.7(4)*
C(71)	0.0917(8)	0.760(1)	0.3256(8)	16.8(6)*
C(72)	0.0889(9)	0.718(2)	0.2900(8)	17.2(8)*
C(73)	0.1268(8)	0.848(1)	0.4082(8)	15.0(8)*
C(74)	0.0855(9)	0.897(2)	0.3815(9)	16.5(7)*
C(75)	0.1902(8)	0.751(1)	0.4052(7)	13.8(9)*
C(76)	0.187(1)	0.692(2)	0.4330(9)	19.9(9)*
Solvent molecules				
O(8)	0.339	0.774	0.477	15.0
C(80)	0.350	0.710	0.459	15.0
O(9)	0.033	0.760	0.166	15.0
C(90)	0.000	0.763	0.100	15.0
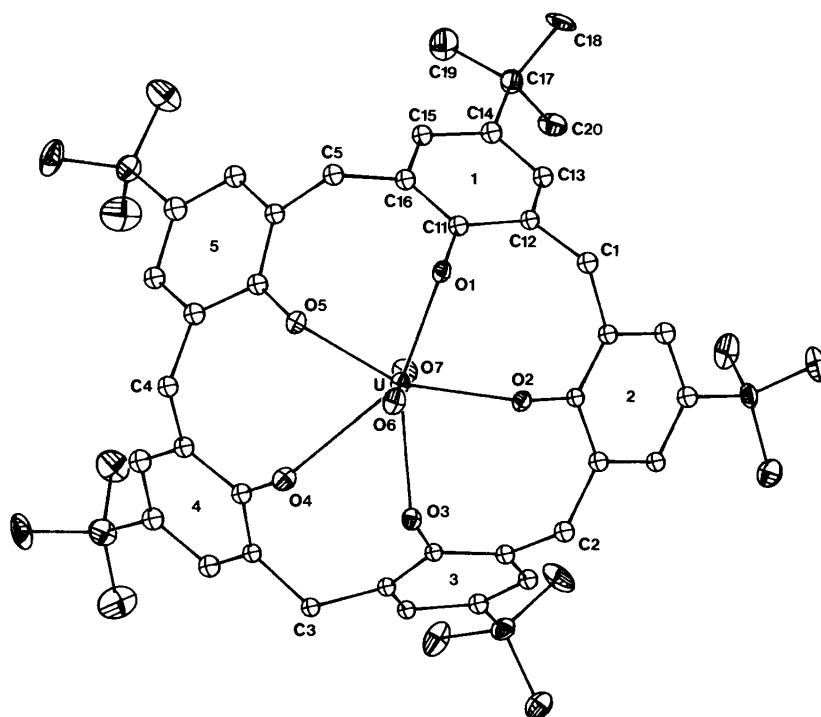
Figure 2. Molecular unit of (**1**). Counterions and solvent molecules omitted. The atom numbering scheme for rings 2–5 is similar to that for ring 1.

The charge of the complex core can be deduced from that of the counterions: two protonated triethylamine molecules are present in the structure (see below), which indicates that four phenolic groups are deprotonated. This situation can be compared to that in bis(homo-oxa)-*p-tert*-butylcalix[4]arene, in which the four phenolic oxygen atoms are deprotonated [1]. To our knowledge, no information is available about the acidity of the phenolic groups in *p-tert*-butylcalix[5]arene, but one can hypothesize that this high degree of deprotonation may be due to an acid-enhancing effect of the uranyl ion, as proposed previously [1]; the unusual deprotonation of four phenolic groups out of six has also been observed previously for *p-tert*-butylcalix[6]arene [5]. In the present case, the three shorter U—O distances are comparable to those observed for deprotonated phenolic oxygen atoms in the uranyl complexes of bis(homo-oxa)-*p-tert*-butylcalix[4]arene (2.24–2.27 (mean value 2.26(1)) Å) [1], *p-tert*-butylcalix[8]arene (2.13–2.31 (mean value 2.21(6)) Å) [2,3] and *p-tert*-butylcalix[6]arene (2.22–2.31 (mean value 2.27(4)) Å) [5]. These three U—O distances can thus reasonably be attributed to deprotonated oxygen atoms and one of the two longer distances must correspond to a protonated oxygen atom, but a clear-cut attribution of the proton to O(3) or O(4) is not possible on the basis of this structure only. The inequivalence of the four bond distances with

Table II. Selected bond distances (Å) and angles (°), with ESD in parentheses.

Uranyl environment			
U—O(1)	2.254(7)	U—O(2)	2.304(7)
U—O(3)	2.571(7)	U—O(4)	2.836(8)
U—O(5)	2.260(7)	U—O(6)	1.782(8)
U—O(7)	1.797(7)		
O(1)—U—O(2)	76.6(2)	O(2)—U—O(3)	78.0(2)
O(3)—U—O(4)	55.2(2)	O(4)—U—O(5)	70.3(2)
O(5)—U—O(1)	80.0(2)	O(6)—U—O(7)	176.1(3)
Hydrogen bonding contacts			
N(1)···O(7)	2.75(2)	N(2)···O(2)	2.72(2)
O(8)···O(3)	2.74(1)	O(9)···O(1)	2.92(1)
Torsion angles			
C(13)—C(12)—C(1)—C(26)	−84(1)	C(25)—C(26)—C(1)—C(12)	93(1)
C(23)—C(22)—C(2)—C(36)	−85(1)	C(35)—C(36)—C(2)—C(22)	73(1)
C(33)—C(32)—C(3)—C(46)	−87(1)	C(45)—C(46)—C(3)—C(32)	99(1)
C(43)—C(42)—C(4)—C(56)	−81(1)	C(55)—C(56)—C(4)—C(42)	79(1)
C(53)—C(52)—C(5)—C(16)	−91(1)	C(15)—C(16)—C(5)—C(52)	82(1)

deprotonated oxygen atoms may indicate that the coordination site is slightly too large for the uranyl ion and that three U—O distances only can be optimal ones. The five oxygen atoms in (**1**) define a plane within ±0.04(1) Å, the uranium atom being at 0.02 Å from this mean plane. The O···O contacts between oxygen atoms pertaining to adjacent phenolic groups range from 2.52(1) to 3.07(1) Å: significantly, the shorter contact, suggesting a strong hydrogen bond, involves the atoms O(3) and O(4).

A triethylammonium ion (corresponding to N(1)) is included within the calixarene cavity: such a situation has already been observed in the complex with bis(homo-oxa)-*p-tert*-butylcalix[4]arene [1]. The other triethylammonium ion (corresponding to N(2)) is located outside the calixarene cavity. The N(1)···O(7) and N(2)···O(2) distances are indicative of possible hydrogen bonds between the nitrogen atoms and a uranyl or a phenolic oxygen atoms respectively, as often observed [1–3,5]. Some differences between (**1**) and the uranyl complex of bis(homo-oxa)-*p-tert*-butylcalix[4]arene arise from the hydrogen bonding contacts: in the latter case, the included triethylammonium ion is hydrogen bonded to a phenolic oxygen atom of an adjacent molecule (which results in the reversing of this ion with respect to the present case) and the non-included counterion is hydrogen bonded to a phenolic oxygen atom *via* a water molecule. In (**1**), two methanol molecules are also present, at distances from the phenolic oxygen atoms O(1) and O(3) compatible with the formation of hydrogen bonds.

The calixarene conformation, which can be characterized by the torsion angles defined by Ugozzoli and Andreetti [19], is the usual *cone* one, as observed, with slight distortions, in the previous structures involving *p-tert*-butylcalix[5]arene and its derivatives [8–12]: up to now, this ligand has appeared to retain this conformation whatever its charge and the nature of substituents and complexed species.

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