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Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(C-C)$ = 0.007 Å
R factor = 0.033
wR factor = 0.065
Data-to-parameter ratio = 16.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

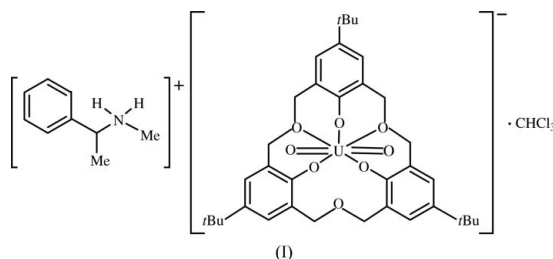
The chloroform-solvated uranyl complex of *p*-tert-butylhexahomotrioxacalix[3]arene with the chiral counter-ion (*S*)-(–)-*N*, α -dimethylbenzylammonium

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In the title compound, (*S*)-(–)-*N*, α -dimethylbenzylammonium dioxo[7,15,23-tri-*tert*-butyl-3,11,19-trioxatetracyclo[19.3.1.1^{5,9}.1^{13,17}]heptacos-1(25),5,7,9(27),13,15,17(26),-21,23-nonaene-25,26,27-triolato]uranate(VI) chloroform solvate, (C₉H₁₄N)[UO₂(C₃₆H₄₅O₆)]·CHCl₃, the uranyl ion is bound to the three phenoxide groups and two of the ether groups of the deprotonated *p*-tert-butylhexahomotrioxacalix[3]arene molecule in a cone conformation, giving a mono-anionic complex. The chiral counter-ion, (*S*)-(–)-*N*, α -dimethylbenzylammonium, is included in the cavity and involved in both a hydrogen bond with the uranyl oxo group directed inwards and an N–H·· π interaction with one of the aromatic rings.

Comment

Complexation of the uranyl ion with *p*-tert-butylhexahomotrioxacalix[3]arene (Masci, 2001; Shokova & Kovalev, 2004) in the presence of triethylamine or DABCO (1,4-diazabicyclo[2.2.2]octane) has been reported previously to give the first example of trigonal coordination geometry for this ion (Thuéry *et al.*, 1999; Thuéry, Nierlich, Harrowfield & Ogden, 2001) [another example of such a geometry, with amide ligands, was described later (Burns *et al.*, 2000)]. This ligand comprises two sets of potential donor atoms, phenoxides and ethers, which are alternately located in two nearly parallel planes. We have shown that the slight conformational changes that occur when the nature of the ammonium counter-ion is changed lead to tetragonal or pentagonal bipyramidal coordination geometries, the extra donor groups being one or two ether O atoms, respectively (Masci *et al.*, 2002*a,b*). The amines used in this work were either primary (butylamine), secondary (dibutylamine, 4-methylpiperidine) or tertiary (tripropylamine, [2.2.2]cryptand). We report here the structure of the complex, (I), obtained with the chiral secondary amine (*S*)-(–)-*N*, α -dimethylbenzylamine. Complexation of a chiral ammonium ion in a capsule built from a derivative of hexahomotrioxacalix[3]arene has previously been reported (Ikeda *et al.*, 2001).



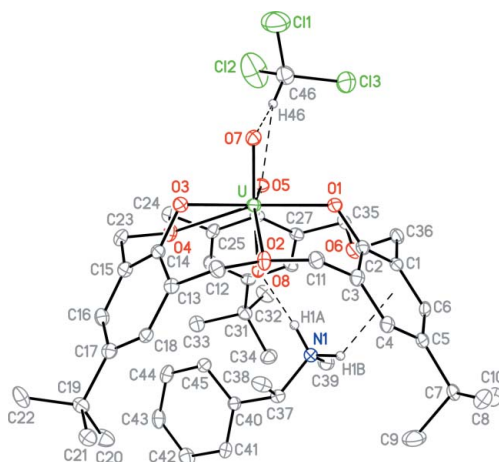


Figure 1

A view of (I), with a partial atom-numbering scheme. The H atoms not involved in intermolecular interactions have been omitted. The hydrogen bonds and N—H... π interaction are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

The asymmetric unit in (I) (Fig. 1) contains one complex anion, one protonated (*S*)-(–)-*N*, α -dimethylbenzylammonium counter-ion and one chloroform molecule. As in the previous uranyl complexes with this macrocycle, the uranyl ion is located at the centre of the homooxalixarene in the cone conformation. It is bound to the three phenoxide atoms O1, O3 and O5 with a mean U—O bond length of 2.228 (6) Å, as usual with this macrocycle, and to ether atoms O2 and O4, with a mean U—O bond length of 2.81 (3) Å, the third ether atom, O6, being non-bonding, at a distance of 3.688 (5) Å. The molecule thus possesses a pseudo-symmetry plane containing the uranyl ion, phenoxide atom O3 and ether atom O6. The U—O_{ether} bond lengths are in good agreement with the value of 2.818 (6) Å found in the analogous complex with the 4-methylpiperidinium cation, in which two ether groups are coordinated. The U—O_{ether} bond lengths in this family of compounds are larger than those observed in the dinuclear uranyl complex of *p*-methyloctahomotetraoxalix[4]arene [mean value 2.67 (2) Å] (Thuéry, Nierlich, Vicens & Masci, 2001) or in the six-coordinated uranyl complexes with crownethers [2.50–2.58 Å] (Thuéry *et al.*, 1995). The U atom environment in (I) is thus a very distorted pentagonal bipyramid, with atoms O2 and O4 displaced by as much as 1.114 (6) and 1.240 (6) Å, respectively, from the plane defined by the three phenoxide O atoms, the U atom being displaced by 0.175 (2) Å from the same plane, on the same side as the ether ligands. The O_{ether}—U—O_{oxo} angles are thus far from 90°, with extreme values of 70.76 (16) and 111.05 (16)° for O4. The O_{phenoxide}—U—O_{phenoxide} angles are larger by about 25° when the O atoms are separated by a coordinated ether bridge.

The three phenol rings make dihedral angles of 50.43 (15), 59.66 (10) and 52.38 (16)° with the phenoxide plane, these values being characteristic of a rather deep cavity, as in the previous compounds. The C—O—C—C torsion angles defined by the ether bridges are all *anti*, in the range 152.9 (6)–168.5 (6)°, typical of nearly planar bridges. However, as previously observed (Masci *et al.*, 2002a), the coordinating

ether O atoms are more displaced than the non-coordinating one with respect to the mean plane defined by the four adjoining C atoms, with values of 0.425 (5), 0.369 (5) and 0.230 (5) Å for O2, O4 and O6, respectively, so that the former come closer to the central metal ion, O6 being by contrast pushed away from it.

The (*S*)-(–)-*N*, α -dimethylbenzylammonium counter-ion is included in the complex cavity and involved in a strong hydrogen bond, with the uranyl oxo atom O8 directed inwards (Table 2), which was also observed with some, but not all, of the ammonium ions investigated previously (in some cases, the hydrogen bonds involve ether or phenoxide groups and/or are mediated by a solvent molecule, whereas, with mono- or dihydro[2.2.2]cryptand, no hydrogen bond is present). The second H atom linked to N1 is likely involved in an N—H... π interaction with the aromatic ring corresponding to phenoxide atom O1 (Table 2). The chloroform solvent molecule is located out of the cavity and is likely involved in a bifurcated hydrogen bond with oxo atom O7 and phenoxide atom O5 (Table 2). No other significant C—H... π or π – π interaction is present in the packing.

Experimental

p-*tert*-Butylhexahomotrioxalix[3]arene was prepared as described in the literature (Dhawan & Gutsche, 1983). For the synthesis of (I), a solution of UO₂(NO₃)₂·6H₂O (15 mg, 0.030 mmol) in MeOH (3 ml) was added dropwise to a stirred and heated mixture of *p*-*tert*-butylhexahomotrioxalix[3]arene (17 mg, 0.029 mmol) and (*S*)-(–)-*N*, α -dimethylbenzylamine (50 mg, 0.37 mmol) in MeOH (5 ml) and CHCl₃ (4 ml). The orange solution was further stirred and heated for 10 min, and dark-orange crystals formed in a few days from the partly evaporated solution.

Crystal data

(C₉H₁₄N)[UO₂(C₃₆H₄₅O₆)]·CHCl₃
M_r = 1099.33
 Orthorhombic, *P*₂₁₂₁
a = 9.6605 (3) Å
b = 21.2825 (10) Å
c = 22.8491 (11) Å
V = 4697.8 (3) Å³
Z = 4
D_x = 1.554 Mg m^{–3}

Mo *K* α radiation
 Cell parameters from 82013 reflections
 θ = 2.6–25.7°
 μ = 3.68 mm^{–1}
T = 100 (2) K
 Platelet, translucent dark orange
 0.14 × 0.12 × 0.04 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: part of the refinement model (ΔF) (DELABS in PLATON; Spek, 2003)
T_{min} = 0.527, *T_{max}* = 0.863

82013 measured reflections
 8750 independent reflections
 8052 reflections with *I* > 2 σ (*I*)
R_{int} = 0.062
 θ_{max} = 25.7°
h = –11 → 11
k = –25 → 25
l = –25 → 27

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.033
wR(*F*²) = 0.065
S = 1.02
 8750 reflections
 543 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0114P)^2 + 4.555P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.003$
 $\Delta\rho_{max} = 0.80 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.83 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983),
 4337 Friedel pairs
 Flack parameter: –0.010 (5)

Table 1

Selected geometric parameters (Å, °).

U—O1	2.224 (3)	U—O5	2.224 (4)
U—O2	2.778 (4)	U—O7	1.791 (3)
U—O3	2.237 (4)	U—O8	1.795 (3)
U—O4	2.833 (3)		
O1—U—O2	68.60 (12)	O1—U—O8	90.60 (13)
O2—U—O3	67.48 (12)	O2—U—O7	109.17 (14)
O1—U—O3	128.72 (14)	O2—U—O8	73.29 (13)
O3—U—O4	66.46 (12)	O3—U—O7	83.68 (15)
O4—U—O5	68.89 (11)	O3—U—O8	100.86 (14)
O3—U—O5	126.69 (13)	O4—U—O7	111.00 (13)
O5—U—O1	102.69 (13)	O4—U—O8	70.82 (13)
O7—U—O8	175.44 (16)	O5—U—O7	86.40 (15)
O1—U—O7	86.83 (14)	O5—U—O8	90.48 (14)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O8	0.90	1.91	2.781 (6)	161
N1—H1B...Cg	0.90	2.68	3.460 (4)	146
C46—H46...O5	0.98	2.31	3.132 (7)	141
C46—H46...O7	0.98	2.36	3.208 (8)	145

The H atoms bound to N1 were found in a difference Fourier map and treated as riding atoms with an isotropic displacement parameter equal to $1.2U_{eq}(N1)$. All other H atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (CH_{arom}), 0.98 (CH), 0.97 (CH₂) or 0.96 Å (CH₃), and isotropic displacement parameters equal to $1.2U_{eq}$ (CH and CH₂) or $1.5U_{eq}$ (CH₃) of the parent atom.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *HKL2000* (Otwinowski & Minor, 1997); data reduction: *HKL2000*;

program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* (Bruker, 1999); *PLATON* (Spek, 2003).

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