

Inclusion of diprotonated [2.2.2]cryptand in the cavity of uranyl-complexed *p*-phenyltetrahomodioxacalix[4]arene

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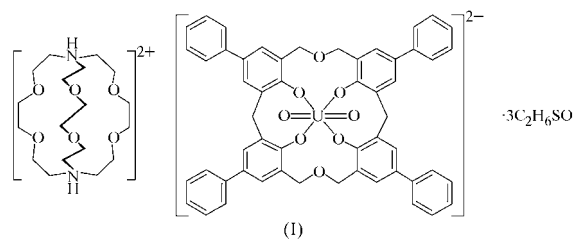
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In the title compound, 4,7,13,16,21,24-hexaoxa-1,10-diazonia-bicyclo[8.8.8]hexacosane dioxo[7,13,21,27-tetraphenyl-3,17-dioxapentacyclo[23.3.1.1^{5,9}.1^{11,15}.1^{19,23}]ditriaconta-1(29),5,7,-9(30),11(31),12,14,19(32),20,22,25,27-dodecaene-29,30,31,32-tetraolato]uranium dimethyl sulfoxide trisolvate, (C₁₈H₃₈N₂O₆)[U(C₅₄H₄₀O₆)O₂]·3C₂H₆OS, the uranyl ion is bound to the four phenoxide groups of the deprotonated *p*-phenyltetrahomodioxacalix[4]arene ligand in a cone conformation, resulting in a dianionic complex. The diprotonated [2.2.2]cryptand counter-ion is located in the cavity defined by the eight aromatic rings of the homooxacalixarene, where it is held by cation–anion, cation– π and possibly C–H·· π interactions. Dimerization in the packing leads to the formation of sandwich assemblages in which two diprotonated [2.2.2]cryptands are encompassed by two uranyl complexes.

Comment

The uranyl complexes of calixarenes and their homo-, homooxa- and homoazacalixarenes derivatives have been widely investigated in the past few years (Harrowfield, 1997; Thuéry, Nierlich, Harrowfield & Ogden, 2001). It has been shown in particular that uranyl complexes of homooxacalixarenes in which at least one methylene bridge is replaced by a –CH₂–O–CH₂– link (Masci, 2001) could be used to build supramolecular architectures. The presence both of a hydrophobic cavity surrounded by aromatic rings, which can be involved in various weak interactions (cation– π and C–H·· π), and of oxo (uranyl), ether and phenoxide groups directed either inside or outside of the cavity provide several sites for counter-ion bonding. Primary, secondary and tertiary ammonium ions can thus give extended assemblages through hydrogen bonds and interactions with the aromatic rings (Masci *et al.*, 2002, 2002*a,b*), whereas alkali metal counter-ions can bind to the uranyl oxo groups to give dimers or infinite

chains (Thuéry & Masci, 2003, 2004). We have reported previously the syntheses and crystal structures of mono-anionic uranyl complexes with *p*-*R*-hexahomotrioxacalix[3]-arene (*R* = *tert*-butyl or phenyl), with protonated [2.2.2]cryptand as counter-ion (Masci *et al.*, 2002*b*). Depending on the stoichiometry, it is possible to obtain two different arrangements, with either the mono-protonated [2.2.2]cryptand nested in the cavity of one complex molecule or its diprotonated form sandwiched by two complexes facing each other. We report here the structure of the analogous complex, (I), with the larger *p*-phenyltetrahomodioxacalix[4]arene. This ligand, as well as the *p*-methyl and *p*-*tert*-butyl derivatives, is known to complex one uranyl ion with its four phenoxide groups, the ether O atoms being non-coordinating (Thuéry, Nierlich, Vicens *et al.*, 2001; Masci *et al.*, 2002; Thuéry & Masci, 2003).



The asymmetric unit in (I) contains one complex dianion, one diprotonated [2.2.2]cryptand and three solvent dimethyl sulfoxide molecules. A view of the dianion and the cryptand is shown in Fig. 1. The uranyl ion lies at the centre of the homooxacalixarene in a cone conformation, and is bound to all four phenoxide O atoms, with a mean U–O bond length of 2.278 (15) Å, as in the previously reported complexes with similar ligands. Ether atoms O3 and O6 are non-bonding, at distances of 3.863 (5) and 3.846 (4) Å, respectively, from the metal centre. The O–U–O angles involving successive phenoxide groups are larger by about 8–13° for the groups separated by an ether link. The U atom is located 0.059 (2) Å from the mean plane defined by the four phenoxide groups (r.m.s. deviation = 0.027 Å), and ether atoms O3 and O6 are 1.784 (7) and 1.679 (7) Å, respectively, from this plane. The four phenol rings make dihedral angles of 38.2 (2), 37.4 (2), 48.3 (2) and 43.0 (2)° with the O₄ mean plane and would define a shallow cavity, similar to those observed in the previous compounds, but for the presence of the *p*-phenyl substituents, which give it additional depth. These phenyl rings are differently oriented with respect to the phenol rings to which they are attached, with dihedral angles of 29.4 (3), 44.13 (17), 13.9 (4) and 49.5 (3)° for the rings bearing atoms O1, O2, O4 and O5, respectively. The torsion angles in the ether bridges are all *anti* [164.3 (5)–170.5 (5)°], which is usual in this family of complexes.

The [2.2.2]cryptand is doubly protonated in the so-called 'in-in' conformation, with the two H atoms pointing inwards (*endo* protonation) and involved in trifurcated hydrogen bonds with the three proximal ether O atoms. This conformation, which is more stable than the 'out-out' one, was also observed in the previous cases (Masci *et al.*, 2002*b*) and precludes any cation–anion interaction through hydrogen

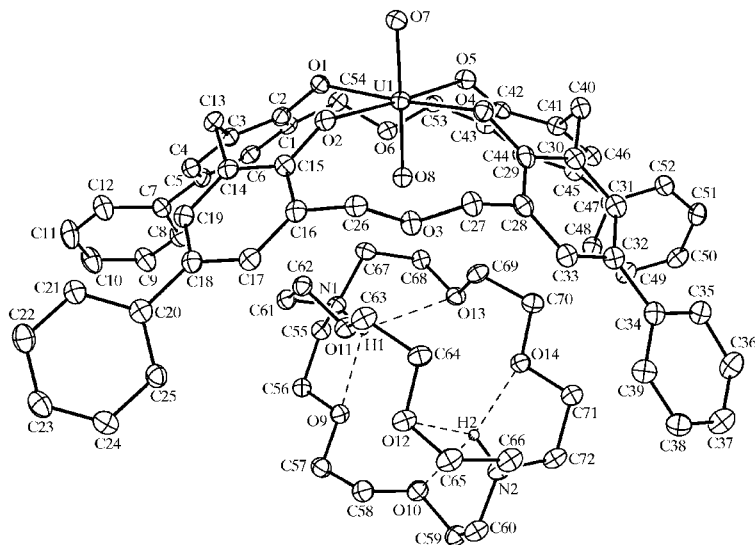


Figure 1

A view of (I), with the atom-numbering scheme. The solvent molecules and the H atoms not involved in hydrogen bonds have been omitted. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

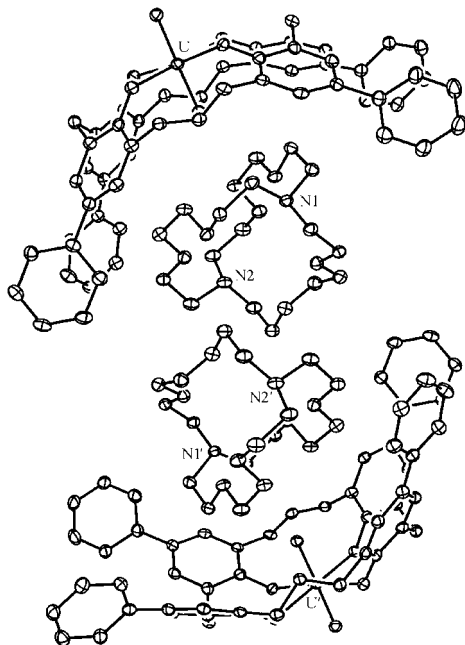


Figure 2

A view of the dimeric assemblage in (I). The solvent molecules and H atoms have been omitted. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (') $1 - x, 1 - y, 2 - z$.]

bonding. The $N1 \cdots N2$ distance, 5.996 (9) Å, is much shorter than in the neutral (6.87 Å; Metz *et al.*, 1976) or mono-protonated cryptand [6.787 (7) and 6.861 (6) Å; Masci *et al.*, 2002b], and is comparable to those in other diprotonated species with analogous geometry [5.710 (7) Å; Thuéry & Masci, 2002]. This shortening of the dication is a result of the presence of six intramolecular hydrogen bonds. The $O \cdots O$ separations in each half-molecule are in the range 3.613 (7)–4.129 (7) Å, and the O9/O11/O13 and O10/O12/O14 planes are nearly parallel, with a dihedral angle of 1.69 (12)° between them. The $N-C-C-O$ and $O-C-C-O$ torsion angles are all *gauche* [45.3 (7)–66.9 (7)°], but three $C-O-C-C$ angles are *gauche* instead of *anti* [67.6 (8), 68.2 (8) and 70.3 (7)°].

These values indicate slight distortions with respect to the ideal geometry, as in the cases cited above.

The diprotonated [2.2.2]cryptand moiety is included in the homooxalixarene cavity in such a way that the angle between its principal axis ($N1 \cdots N2$ line) and the uranyl ion axis is 117°. This tilting is at variance with the nearly parallel arrangement found in the case of the narrower cavity of the uranyl complexes of hexahomotrioxalix[3]arene derivatives. Electrostatic cation–anion interactions are likely to contribute to the cohesion of the assembly, but other weak interactions may be discerned as well. The presence of cation– π interactions (Ma & Dougherty, 1997) is suggested by the occurrence of short contacts between aromatic rings and the protonated N atoms or their α -C atoms (Masci *et al.*, 2002b). The shortest contacts are between two of the C atoms bound to N1 (C61 and C67), and the centroid of the phenol ring bearing O1 (3.77 and 4.00 Å, respectively), whereas the distance between N1 and this centroid is 4.47 Å. These distances agree with those measured in similar (Masci *et al.*, 2002, 2002b) and different systems (Verdonk *et al.*, 1993; Murayama & Aoki, 1997). The C atoms bound to atom N2 are farther from aromatic centroids, with the shortest contact being 4.35 Å between atom C66 and the *p*-phenyl ring attached to the phenolate ring bearing atom O4. Some $C-H \cdots \pi$ interactions may also be present; the three shortest contacts are reported in Table 2. Two C atoms of the dimethyl sulfoxide solvent molecules may also be involved in $C-H \cdots \pi$ interactions.

The packing brings together two cation–anion units related by the inversion centre at $(\frac{1}{2}, \frac{1}{2}, 0)$ in such a manner that the ensemble can be viewed as two homooxalixarene uranyl complexes including two diprotonated [2.2.2]cryptands (Fig. 2). After the 1:1 and 2:1 complex/cryptand stoichiometries previously encountered, the 2:2 dimeric assemblage described here is a new example of the versatility of such systems in supramolecular chemistry. However, by contrast with the previous cases in which the sandwich assemblages

are held by cation–anion, cation– π and C–H... π interactions (with sufficient strength for the species characterized in the solid state to be stable in solution), the two halves of the dimer in (I) are likely to be held together by van der Waals forces alone.

Experimental

p-Phenyltetrahomodioxacalix[4]arene was prepared as described by No (1999). For the synthesis of (I), a 0.20 M solution of UO₂(NO₃)₂·6H₂O in MeOH (30 ml) was added dropwise to a stirred and heated mixture of *p*-phenyltetrahomodioxacalix[4]arene (8.0 mg, 0.010 mmol) and [2.2.2]cryptand (4.1 mg, 0.011 mmol) in CHCl₃ (5 ml). Stirring and heating were continued for 10 min. The red powder obtained on complete solvent evaporation was recovered, washed with acetone and dissolved in gently heated Me₂SO. Light-orange crystals of complex (I) formed over a period of a few days.

Crystal data

(C₁₈H₃₈N₂O₆)[U(C₅₄H₄₀O₆)O₂]-3C₂H₆OS
M_r = 1667.78
 Monoclinic, *P*₂₁/*n*
a = 14.8955 (5) Å
b = 20.3681 (10) Å
c = 24.9276 (11) Å
 β = 106.169 (3)°
V = 7263.7 (5) Å³
Z = 4

D_x = 1.525 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 190557 reflections
 θ = 2.9–25.7°
 μ = 2.39 mm⁻¹
T = 100 (2) K
 Irregular, translucent light-orange
 0.15 × 0.14 × 0.10 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} = 0.603, *T_{max}* = 0.787

190557 measured reflections
 13724 independent reflections
 10606 reflections with *I* > 2 σ (*I*)
R_{int} = 0.082
 θ_{max} = 25.7°
h = 0 → 18
k = 0 → 24
l = -30 → 29

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.052
wR (*F*²) = 0.146
S = 1.04
 13724 reflections
 922 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/[$\sigma^2(F_o^2) + (0.0659P)^2 + 43.6206P$]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 $\Delta\rho_{max}$ = 2.54 e Å⁻³
 $\Delta\rho_{min}$ = -1.26 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

U1–O1	2.288 (4)	U1–O5	2.254 (4)
U1–O2	2.292 (4)	U1–O7	1.794 (5)
U1–O4	2.277 (5)	U1–O8	1.778 (4)
O1–U1–O2	82.39 (16)	O2–U1–O8	91.10 (18)
O2–U1–O4	95.26 (16)	O4–U1–O7	89.09 (19)
O4–U1–O5	87.27 (17)	O4–U1–O8	92.46 (19)
O5–U1–O1	94.96 (17)	O5–U1–O7	89.69 (19)
O1–U1–O7	86.57 (19)	O5–U1–O8	90.47 (18)
O1–U1–O8	91.88 (18)	O8–U1–O7	178.4 (2)
O2–U1–O7	88.67 (18)		

H atoms bound to N atoms were found in difference Fourier maps and refined with isotropic displacement parameters set equal to 1.2*U_{eq}* of the parent atom. All other H atoms were introduced at

Table 2

Hydrogen-bond geometry (Å, °).

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C6, C41–C46 and C34–C39 rings, respectively.

<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–H1...O9	0.92 (8)	2.24 (7)	2.647 (7)	106 (6)
N1–H1...O11	0.92 (8)	2.28 (8)	2.756 (8)	112 (6)
N1–H1...O13	0.92 (8)	2.50 (8)	2.901 (8)	107 (5)
N2–H2...O10	0.95 (8)	2.53 (8)	2.892 (8)	103 (5)
N2–H2...O12	0.95 (8)	2.55 (8)	2.895 (8)	101 (5)
N2–H2...O14	0.95 (8)	2.20 (8)	2.718 (8)	113 (6)
C61–H61B... <i>Cg</i> 1	0.97	2.97	3.77	141
C69–H69B... <i>Cg</i> 2	0.97	2.64	3.56	159
C71–H71A... <i>Cg</i> 3	0.97	2.66	3.52	148

calculated positions as riding atoms, with C–H bond lengths of 0.93 (CH), 0.97 (CH₂) or 0.96 Å (CH₃), and isotropic displacement parameters equal to 1.2*U_{eq}* (CH and CH₂) or 1.5*U_{eq}* (CH₃) of the parent atom. Restraints on displacement parameters were applied for atoms S2, O16, C73 and C77 of the badly resolved solvent molecules.

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 and PLATON (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1098). Services for accessing these data are described at the back of the journal.

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