Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Bis{bis[5-*tert*-butyl-2-oxido-3-(1-pyridiniomethyl)phenyl]methane}dioxouranium bis(trifluoromethanesulfonate) pyridine disolvate: a uranyl bis(diphenoxide) complex resulting from homooxacalixarene cleavage

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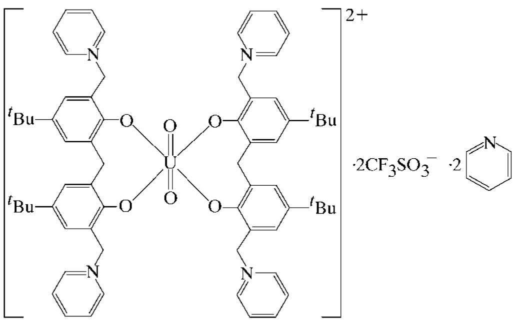
Received 7 November 2003
Accepted 1 December 2003
Online 13 December 2003

The title compound, $[UO_2(C_{33}H_{38}N_2O_2)_2](CF_3SO_3)_2\cdot 2C_5H_5N$, has been obtained by reaction of $U^{IV}$ trifluoromethanesulfonate with *p-tert*-butyltetrahomodioxacalix[4]arene in pyridine. The uranyl ion lies on an inversion centre and is bound to two O atoms from each diphenoxide ligand, which gives the usual square-planar equatorial environment. The zwitterionic diphenoxide species results from nucleophilic attack by pyridine on the benzylic ether C atoms of the homooxacalixarene, assisted by initial U coordination to the ether groups, with subsequent metal oxidation giving the uranyl moiety.

## Comment

In their polyphenoxide form, homooxacalixarenes (Masci, 2001), as well as the more widespread calixarenes, are ligands well suited to uranyl ion [dioxouranium(VI)] complexation (Thuéry *et al.*, 2001). In order to extend the investigation of uranium complexes of homooxacalixarenes to lower oxidation states of this cation, we have recently studied the reaction of $UCl_4$ with *p-tert*-butyltetrahomodioxacalix[4]arene, *p-tert*-butylhexahomotrioxacalix[6]arene and *p-tert*-butyloctahomotetraoxacalix[8]arene in pyridine, with the unexpected result of homooxacalixarene cleavage to give the diphenoxide species bis[5-*tert*-butyl-2-oxido-3-(1-pyridiniomethyl)phenyl]methane (*L*) and subsequent isolation of the 1:1 or 1:2 $U^{IV}/L$ complexes (Salmon *et al.*, 2003). The proposed mechanism involves nucleophilic attack by pyridine on the ether bridges, likely assisted by initial U coordination to the ether O atoms. In the course of a similar study with $U(OSO_2CF_3)_4$ and *p-tert*-butyltetrahomodioxacalix[4]arene as starting materials, further oxidation of the metal centre, due either to oxygen contamination or the presence of water released by the cleavage reaction, resulted in the isolation of the present uranyl complex, (I), and its structure is presented here.



(I)

The asymmetric unit in (I) contains half a complex molecule, with the U atom located on a centre of symmetry, a trifluoromethanesulfonate counter-ion and a pyridine solvent molecule. The U atom is bound (Fig. 1, Table 1) to two phenoxide (PhO) O atoms from each neutral doubly zwitterionic ligand, with a mean U—O bond length of 2.256 (6) Å, typical of such phenoxide complexes (Thuéry *et al.*, 2001). The $O_{PhO}—U—O_{PhO}$ and $O_{oxo}—U—O_{PhO}$ angles are close to 90° [87.85 (14)–92.15 (14)°], and the equatorial environment of the uranyl ion is thus a rather regular square.

We have previously reported the crystal structure of the 1:2 uranyl complex, (II), of another diphenoxide species, in which the cationic pyridiniomethyl groups present in *L* are replaced by neutral hydroxymethyl substituents. The structure of (II) comprises three independent molecules, either centrosymmetric or pseudo-centrosymmetric, in which the U environment is close to that in (I); in one of these molecules, however, this environment is somewhat less regular, due to the presence of an intramolecular $O_{OH}\cdots O_{PhO}$ hydrogen bond between the two ligands (Thuéry *et al.*, 2002). The two diphenoxide rings in (I), as well as those in (II), adopt a 'butterfly' conformation

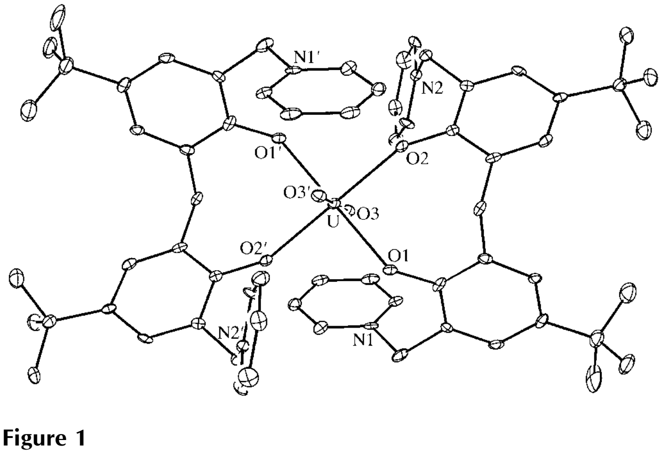


**Figure 1**
A view of complex (I), with a partial atom-numbering scheme. The counter-ions, H atoms and solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Primed atoms are at the symmetry position (2 − *x*, 1 − *y*, 1 − *z*).

DOI: 10.1107/S0108270103027513

and are located on either side of the uranyl equatorial plane. The dihedral angles in (I) between the two phenoxide rings of each ligand and this plane are 43.94 (14) and 25.8 (2)° and, between the two phenoxide rings, 69.66 (17)°, whereas the corresponding values in (II) are 36.9 (6)–52.4 (5)° and 71.4 (6)–79.6 (7)°, respectively. The ligand *L* in its 1:1 and 1:2 $\mathrm{U^{IV}}$ complexes adopts a similar conformation, with dihedral angles between the two aromatic rings larger than in (I), at 76.3 (2) and 76.2 (4)°. Even if these diphenoxide species give complexes with comparable overall arrangements, the differences in finer geometric details evidence the flexibility of these ligands and their ability to adapt themselves to differing coordination requirements (as between $\mathrm{U^{IV}}$ and $\mathrm{U^{VI}}$ cations) or differing weak interactions.

The two pyridiniomethyl arms of each ligand in (I) are directed away from the uranyl equatorial plane, *i.e.* towards the concave side of the diphenoxide ligand. The aromatic ring containing atom N2 is involved in two weak but significant $\pi$–$\pi$ stacking interactions, one with its counterpart in the neighbouring molecule at $(1 - x, 1 - y, 1 - z)$ (centroid–centroid distance = 3.59 Å, interplanar spacing = 3.38 Å, and centroid offset = 1.21 Å) and the other, weaker, with the solvent pyridine molecule [centroid–centroid distance = 4.00 Å, interplanar spacing = 3.58 Å, centroid offset = 1.78 Å, dihedral angle between the two rings = 10.51 (17)°, and shortest interatomic contact C29$\cdots$C36 = 3.368 (9) Å, equal to twice the out-of-plane van der Waals radius of C (1.7 Å)].

The pyridine solvent molecule is located in the 'cup' defined by the two phenoxide rings of the ligand (Fig. 2), in which it is held by two C—H$\cdots\pi$ interactions, the first between atom H35 and the C1–C6 aromatic ring bound to atom O1 (H35–centroid distance = 2.90 Å and C35—H35–centroid angle = 173°), and the second between atom H36 and the C12–C17 aromatic ring bound to atom O2 (H36–centroid distance = 2.77 Å and C36—H36–centroid angle = 148°). In the previous uranyl ion complex with a diphenoxide species, (II), a comparable position was occupied by an HDABCO cation (DABCO is 1,4-diazabicyclo[2.2.2]octane), but in that case the cation was primarily held by a strong N—H$\cdots$O$_{\mathrm{oxo}}$ hydrogen bond with the central uranyl ion and by cation–$\pi$ interactions involving the phenoxide rings (Thuéry *et al.*, 2002). Another weak C—H$\cdots\pi$ interaction may be considered in (I), between an H atom of the *tert*-butyl group bound to the phenoxide ring bearing atom O2 and the pyridine molecule at $(1 - x, 1 - y, -z)$ (H19*C*–centroid distance = 2.89 Å and C19—H19*C*–centroid angle = 155°).

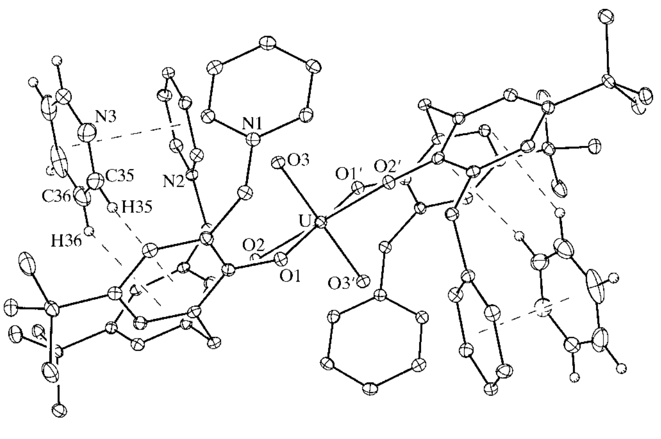


**Figure 2**
A view of complex (I) including the pyridine solvent molecules. The $\pi$–$\pi$ and C—H$\cdots\pi$ interactions are represented as dashed lines. The counter-ions and H atoms (except those of the pyridine molecules) have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Primed atoms are at the symmetry position $(2 - x, 1 - y, 1 - z)$.

The present result provides a new example of homooxacalixarene cleavage in the presence of pyridine and $\mathrm{U^{IV}}$ salts, $\mathrm{UCl_4}$ being replaced in this case by $\mathrm{U(OSO_2CF_3)_4}$. Further oxidation of the metal centre leads to the second example of a diphenoxide complex of the uranyl ion. However, we have also reported that some triphenols complex this ion in their diphenoxide form (Thuéry *et al.*, 2002, and references therein). Direct reaction of uranyl salts with *p*-*R*-tetrahomodioxacalix[4]arene (where *R* is methyl, *tert*-butyl or phenyl), in the presence of bases such as amines or alkali metal hydroxides, does not result in homooxacalixarene cleavage, even in the presence of pyridine. In these cases, 'internal' tetraphenoxide-coordinated uranyl complexes are obtained, which differ in their counter-ions, solvent environment and supramolecular arrangement (Thuéry & Masci, 2003, and references therein). The homooxacalixarene in all these complexes is in a cone conformation and, as a consequence, all the phenoxide rings are on the same side of the uranyl equatorial plane, which is at variance with the centrosymmetrical geometry of complex (I). In these homooxacalixarene complexes, the mean U—O$_{\mathrm{PhO}}$ bond length of 2.28 (2) Å (eight compounds) appears slightly larger, albeit with little significance, than that in (I) or in the previous uranyl diphenoxide complex, (II) [2.25 (2) Å], which may be due to the geometrical constraints imposed by the cyclic nature of the homooxacalixarene. The range of O$_{\mathrm{PhO}}$—U—O$_{\mathrm{PhO}}$ angles is also larger in the macrocyclic complexes [82.1 (3)–97.7 (3)°], in conjunction with very different O$\cdots$O distances between adjacent phenoxide groups [mean values of 3.10 (2) Å for groups separated by a methylene link and 3.34 (3) Å for groups separated by an ether link, compared with O1$\cdots$O2 = 3.171 (5) Å and O1$\cdots$O2′ = 3.209 (5) Å in (I)], which is due to the presence of the two ether links, which act as spacers.

## Experimental

*p-tert*-Butyltetrahomodioxacalix[4]arene was synthesized according to the method of Dhawan & Gutsche (1983), and $\mathrm{U(OTf)_4}$ (OTf is $\mathrm{OSO_2CF_3}$) was synthesized according to the method of Berthet *et al.* (1999). Complex (I) was synthesized by reaction of *p-tert*-butyltetrahomodioxacalix[4]arene with one equivalent of $\mathrm{U(OTf)_4}$ in pyridine. The oxidation of the metal centre from $\mathrm{U^{IV}}$ to $\mathrm{U^{VI}}$, in the form of the uranyl ion, can be attributed either to adventitious traces of oxygen, possibly entering the reaction flask during prolonged heating at 383 K or to the water molecules eliminated during nucleophilic attack on the benzylic C atoms by pyridine. Single crystals of (I) were obtained by slow diffusion of tetrahydrofuran into the mother solution.

m28 Lionel Salmon *et al.* • $\mathrm{[UO_2(C_{33}H_{38}N_2O_2)_2](CF_3SO_3)_2\cdot 2C_5H_5N}$ *Acta Cryst.* (2004). C**60**, m27–m29

### *Crystal data*

$[UO_2(C_{33}H_{38}N_2O_2)_2](CF_3SO_3)_2\cdot 2C_5H_5N$
$M_r = 1715.68$
Triclinic, $P\bar{1}$
$a = 10.7189\ (9)$ Å
$b = 11.1479\ (13)$ Å
$c = 17.0975\ (16)$ Å
$\alpha = 102.472\ (6)^\circ$
$\beta = 106.903\ (6)^\circ$
$\gamma = 94.800\ (6)^\circ$
$V = 1885.0\ (3)$ Å$^3$
$Z = 1$
$D_x = 1.511$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 13 391 reflections
$\theta = 2.5$–$25.7^\circ$
$\mu = 2.29$ mm$^{-1}$
$T = 100\ (2)$ K
Needle, light orange
0.40 × 0.10 × 0.05 mm

### *Data collection*

Nonius KappaCCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.698$, $T_{\rm max} = 0.892$
13 391 measured reflections
6934 independent reflections
5444 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.089$
$\theta_{\rm max} = 25.7^\circ$
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 12$
$l = -20 \rightarrow 20$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.096$
$S = 1.03$
6934 reflections
481 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 1.54$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -2.30$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| U—O1 | 2.252 (3) | U—O3 | 1.790 (3) |
| U—O2 | 2.260 (3) | | |
| O1—U—O2 | 89.33 (12) | O2—U—O3 | 87.85 (14) |
| O1—U—O3 | 90.75 (14) | | |

The H atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (CH), 0.97 ($CH_2$) and 0.96 Å ($CH_3$), and with $U_{\rm iso}({\rm H}) = 1.2$ (CH or $CH_2$) or 1.5 ($CH_3$) times $U_{\rm eq}$ of the parent atom. Some restraints on displacement parameters were applied for two F atoms and for the C atoms of the pyridine molecule. The highest positive and negative electron-density residuals are located 0.87 and 0.95 Å, respectively, from the U atom.

Data collection: *EvalCCD* (Duisenberg *et al.*, 2003); cell refinement: *EvalCCD*; data reduction: *EvalCCD*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1040). Services for accessing these data are described at the back of the journal.

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