Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

2,2′-Iminobis(ethanaminium) (*p*-methyldihomooxacalix[4]arene)dioxouranium methanol disolvate monohydrate

Bernardo Masci[a] and Pierre Thuéry[b]*

[a]Dipartimento di Chimica and IMC-CNR, Università 'La Sapienza', Box 34, Roma 62, P.le Aldo Moro 5, 00185 Roma, Italy, and [b]CEA/Saclay, DSM/DRECAM/SCM (CNRS URA 331), Bâtiment 125, 91191 Gif-sur-Yvette, France

Correspondence e-mail: pierre.thuery@cea.fr

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.005 Å
R factor = 0.024
wR factor = 0.059
Data-to-parameter ratio = 15.6

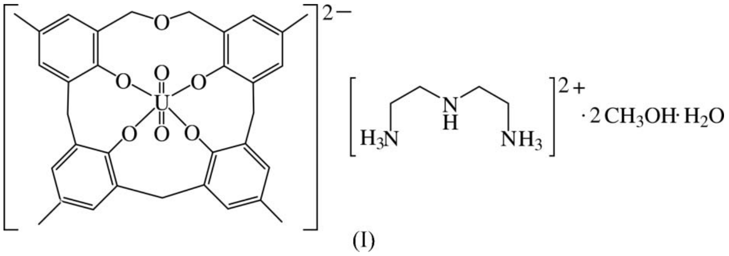
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 21 November 2006
Accepted 28 November 2006

In the title compound, $(C_4H_{15}N_3)[UO_2(C_{33}H_{30}O_5)]\cdot 2CH_3OH\cdot H_2O$, the uranyl ion is bound to the four phenoxide groups of the deprotonated *p*-methyldihomooxacalix[4]arene in the usual cone conformation, giving a dianionic complex. The diprotonated diethylenetriamine counter-ion links neighbouring complex anions along the *b* axis through hydrogen bonding with the oxo, phenoxide and ether groups. The solvent molecules are also involved in hydrogen bonding.

Comment

The complex formed by the uranyl ion with *p*-*tert*-butyldihomooxacalix[4]arene was the first uranyl–calixarene complex to be characterized (Harrowfield *et al.*, 1991), this family having later been extended to include many calixarene derivatives (Thuéry *et al.*, 2001). In recent years, we have investigated the uranyl complexes formed with homooxacalixarenes of varying size (Masci, 2001) in the presence of primary, secondary and tertiary amines (Masci *et al.*, 2002*a*,*b*; Masci *et al.*, 2005; Masci & Thuéry, 2005*a*,*b*). The structure of the uranyl complex with *p*-methyldihomooxacalix[4]arene obtained in the presence of diethylenetriamine as a base and crystallized as a methanol and water solvate, (I), is reported here.



(I)

The asymmetric unit in (I) (Fig. 1) contains one complex dianion, one diprotonated diethylenetriamine counter-ion, two methanol and one water molecules. The uranyl ion is bound to the four phenoxide groups of the macrocycle, which is in a cone conformation, with an average U1—O(phenoxide) bond length of 2.270 (7) Å; this value is 2.258 (11) Å in the *tert*-butyl derivative, (II) (Harrowfield *et al.*, 1991). The U1···O(ether) contact is clearly non-bonding at 3.510 (2) Å [3.534 (8) Å in (II)]. The complex possesses a pseudo-mirror plane containing the uranyl ion and ether atom O5.

In the counter-ion, diethylenetriamine is protonated at its terminal groups and is involved in several hydrogen bonds, both intra- and intermolecular (Table 1). The central amine group (N1) is an acceptor from the two terminal ammonium groups (N2 and N3). Atom N2, which is most embedded in the

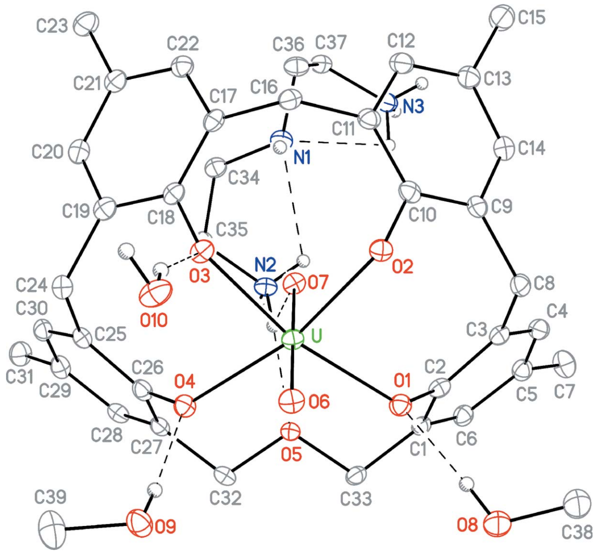


Figure 1
The asymmetric unit of compound (I), showing the atom-numbering scheme. C-bound H atoms have been omitted. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as spheres of arbitrary radii.

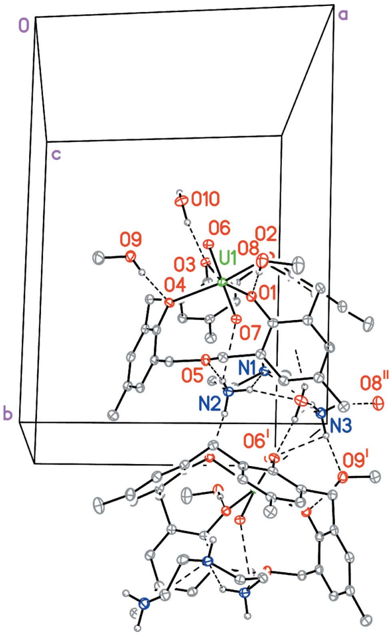


Figure 2
The columnar arrangement in (I). C-bound H atoms are omitted. Hydrogen bonds and C—H$\cdots\pi$ interactions are shown as dashed lines. [Symmetry codes: (i) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$.]

macrocycle cavity, is also a donor to oxo atom O7 and ether atom O5 of the proximal calixarene (bifurcated bond), phenoxide atom O2 of another calixarene and water atom O10. The ammonium group containing N3 points outwards and is a donor to oxo atom O6 of the neighbouring complex along the *b* axis and atoms O8, O9 and O10 of methanol and water molecules. Adjacent complex anions along the *b* axis are thus linked by an intricate hydrogen-bonding network, forming a columnar arrangement of calixarenes tilted by 82.55 (4)° with respect to one another (Fig. 2). The two methanol and the water solvent molecules are hydrogen-bond donors to phenoxide O atoms and, in the case of the water molecule, the second proton is involved in a weak O—H$\cdots\pi$ interaction with the aromatic ring C1–C6 (Table 1).

Experimental

A solution of $UO_2(NO_3)_2\cdot6H_2O$ (12.5 mg, 0.025 mmol) in MeOH (1 ml) was added dropwise to a stirred and heated mixture of *p*-methyldihomooxacalix[4]arene (13.0 mg, 0.025 mmol) (whose synthesis will be reported elsewhere), diethylenetriamine (15 mg, 0.15 mmol), chloroform (4 ml) and MeOH (6 ml). Light-orange crystals of (I) separated on standing.

Crystal data

$(C_4H_{15}N_3)[UO_2(C_{33}H_{30}O_5)]\cdot2CH_4O\cdot H_2O$
$M_r = 963.89$
Monoclinic, $P2_1/n$
$a = 11.9895\ (4)$ Å
$b = 16.2079\ (3)$ Å
$c = 21.2475\ (6)$ Å
$\beta = 105.441\ (2)^\circ$
$V = 3979.88\ (19)$ Å^3
$Z = 4$
$D_x = 1.609$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 4.14$ mm^{-1}
$T = 100\ (2)$ K
Platelet, translucent light orange
0.21 × 0.15 × 0.07 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.528$, $T_{\max} = 0.749$
131799 measured reflections
7565 independent reflections
6173 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 25.7^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.059$
$S = 1.03$
7565 reflections
484 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -1.00$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

Cg is the centroid of atoms C1–C6.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O8—H8$\cdots$O1	0.87	1.88	2.745 (3)	177
O9—H9$\cdots$O4	0.83	1.87	2.688 (3)	170
O10—H10$A\cdots$O3	0.95	1.81	2.715 (3)	160
N2—H2$B\cdots$N1	0.87	2.37	2.834 (4)	114
N2—H2$A\cdots$O7	0.88	2.60	2.975 (3)	106
N2—H2$A\cdots$O5	0.88	2.16	3.034 (3)	173
N2—H2$C\cdots$O2$^{\rm i}$	0.92	1.88	2.788 (3)	169
N2—H2$B\cdots$O10$^{\rm i}$	0.87	2.21	3.000 (4)	151
N3—H3$A\cdots$N1	0.96	2.56	2.929 (4)	103
N3—H3$C\cdots$O6$^{\rm i}$	0.97	2.61	2.950 (3)	101
N3—H3$B\cdots$O8$^{\rm ii}$	0.81	2.16	2.797 (4)	136
N3—H3$C\cdots$O9$^{\rm i}$	0.97	1.85	2.816 (4)	170
N3—H3$A\cdots$O10$^{\rm i}$	0.96	1.96	2.883 (3)	160
O10—H10b$\cdots Cg^{\rm iii}$	0.84	2.67	3.47	160

Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

The H atoms bound to N and O atoms were found in a difference Fourier map and treated as riding atoms with an isotropic displacement parameter equal to $1.2U_{eq}$ of the parent atom. All other H atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (aromatic), 0.97 (CH_2) or 0.96 Å (CH_3), and isotropic displacement parameters equal to $1.2U_{eq}$(CH and CH_2) or $1.5U_{eq}$(CH_3) of the parent atom.

Data collection: *COLLECT* (Nonius, 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) and *PLATON* (Spek, 2003).

References

Bruker (1999). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

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

Masci, B. (2001). *Calixarenes 2001*, edited by Z. Asfari, V. Böhmer, J. M. Harrowfield & J. Vicens, pp. 235–249. Dordrecht: Kluwer Academic Publishers.

Masci, B., Levi Mortera, S. & Thuéry, P. (2005). *Acta Cryst.* C**61**, m482–m484.

Masci, B., Nierlich, M. & Thuéry, P. (2002*a*). *New J. Chem.* **26**, 120–128.

Masci, B., Nierlich, M. & Thuéry, P. (2002*b*). *New J. Chem.* **26**, 766–774.

Masci, B. & Thuéry, P. (2005*a*). *Acta Cryst.* E**61**, m2278–m2280.

Masci, B. & Thuéry, P. (2005*b*). *New J. Chem.* **29**, 493–498.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Thuéry, P., Nierlich, M., Harrowfield, J. & Ogden, M. (2001). *Calixarenes 2001*, edited by Z. Asfari, V. Böhmer, J. M. Harrowfield & J. Vicens, pp. 561–582. Dordrecht: Kluwer Academic Publishers.