Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Crystal structure of an uranyl/*p*-*tert*-butyl calix[6]arene dimer

Pierre Thuéry[a]; Monique Lance[a]; Martine Nierlich[a]
[a] CEA/Saclay, SCM (CNRS URA 331), France

To cite this Article Thuéry, Pierre , Lance, Monique and Nierlich, Martine(1996) 'Crystal structure of an uranyl/*p-tert*-butyl calix[6]arene dimer', Supramolecular Chemistry, 7: 3, 183 — 185

To link to this Article: DOI: 10.1080/10610279608027514

URL: http://dx.doi.org/10.1080/10610279608027514

SUPRAMOLECULAR CHEMISTRY, 1996, Vol. 7, pp. 183–185
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands under license by
Gordon and Breach Science Publishers SA
Printed in Malaysia

Crystal structure of an uranyl/*p-tert*-butyl calix[6]arene dimer

PIERRE THUÉRY*, MONIQUE LANCE and MARTINE NIERLICH

CEA/Saclay, SCM (CNRS URA 331), Bât.125, 91191 Gif-sur-Yvette, France.

(Received October 6, 1995)

The crystal structure of [UO$_2$(*p-tert*-butylcalix[6]arene-4H)]$_2$.(HNEt$_3$)$_2$.(H$_3$O)$_2$.6CH$_3$CN is described. This compound crystallizes in the monoclinic space group P2$_1$/n with $a = 19.183(5)$, $b = 17.726(9)$, $c = 23.206(9)$ Å, $\beta = 106.16(3)°$, $V = 7579(5)$ Å^3, $Z = 2$. 414 parameters were refined to a residual of 0.062 for 3475 observed reflections ($I > 3\sigma(I)$). Two four-fold deprotonated calixarene moieties face each other and are held together by two uranyl ions, each of them bonded to two deprotonated phenolic oxygen atoms of each calixarene moiety (uranyl equatorial geometry, approximately square planar). Two protonated triethylamine molecules form possible hydrogen-bonds with two calixarene oxygen atoms. A hydronium ion is located in each calixarene cavity and forms possible hydrogen bonds with the uncomplexed phenolic oxygen atoms and the nitrogen atom of an acetonitrile molecule.

Few crystal structures of actinide complexes of calixarenes have been reported up to now,[1–4] despite the interest in water-soluble modified calixarenes as "uranophiles"[5]. Harrowfield *et al.* reported the first structure of an uranyl complex, with bis(homo-oxa)-*p-tert*-butylcalix[4]arene[1], in which the uranyl ion is bonded to the four deprotonated phenolic oxygen atoms of the calixarene. Recently, we have described the structure of two phases of a bimetallic complex of uranyl with *p-tert*-butylcalix[8]arene[3,4], in which the two uranyl ions are bonded to four calixarene oxygen atoms (two protonated and two deprotonated) and one bridging hydroxyl ion. Molecular modeling calculations suggest the possibility of including the uranyl ion in the calix[5]- and calix[6]arene cavities[6], but the structures of such complexes have not yet been described. We report here the structure of a dimeric uranyl/*p-tert*-butylcalix[6]arene complex.

The structure determination gives the overall formula $[(UO_2^{2+})(H_2L^{4-})]_2.(HNEt_3^+)_2.(H_3O^+)_2.6CH_3CN$ (where L^{6-} is the hexaanion of *p-tert*-butylcalix[6]arene). The asymmetric unit contains half of the dimeric unit, which is located around a symmetry center. ORTEPII[7] drawings showing the molecular unit and the location of the counter-ions are represented in Figures 1 and 2. Each uranyl ion is bonded to four oxygen atoms (two from each calixarene moiety), with distances ranging from 2.22(1) to 2.31(1) (mean value 2.27(4)) Å. This four-coordinate equatorial geometry contrasts with the five-coordinate one frequently observed, in particular in the bimetallic complex with *p-tert*-butylcalix[8]arene[3,4]. Some other examples of this rare geometry have been reported[1,8]. In particular, it is observed in the complex

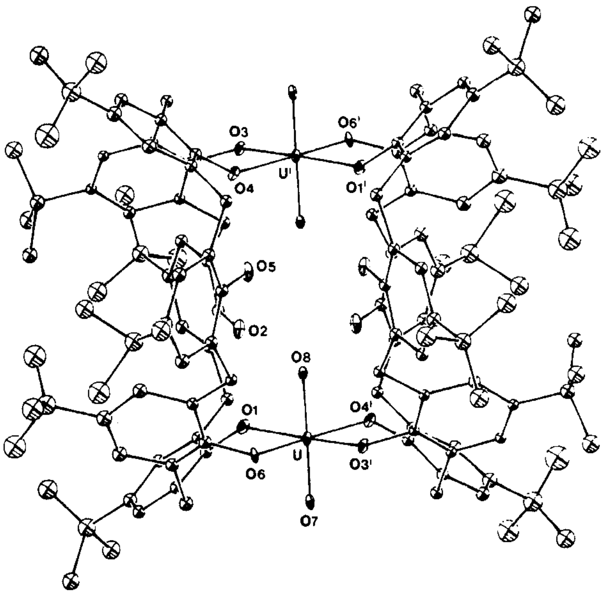

Figure 1 ORTEPII drawing of the title complex (counter-ions and solvent molecules omitted for clarity, disorder on the *tert*-butyl groups not shown). Thermal ellipsoids drawn at the 11% probability level. i = −x, −y, −z. Selected important distances (Å) and angles (°): U-O1 2.28(1), U-O3^i 2.22(1), U-O4^i 2.27(1), U-O6 2.31(1), U-O7 1.72(1), U-O8 1.77(1) Å, O1-U-O4^i 97.3(5), O4^i-U-O3^i 87.8(5), O3^i-U-O6 82.9(5), O6-U-O1 91.9(5), O7-U-O8 177.0(6)°.

---

*To whom correspondence should be addressed.

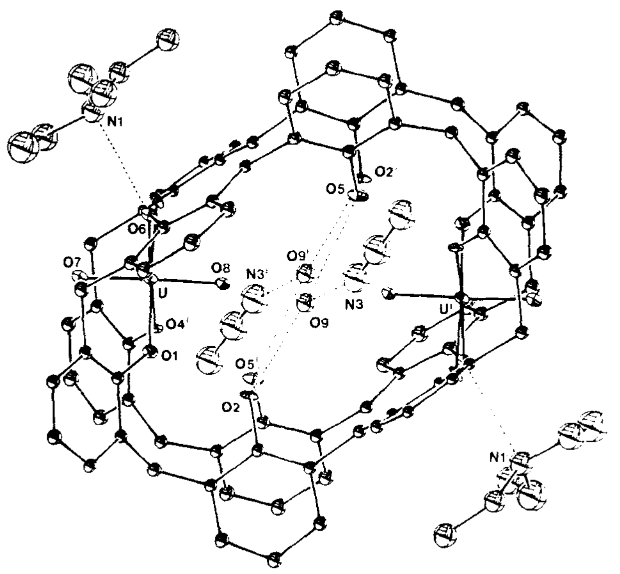

Figure 2 ORTEPII drawing of the title complex including the counter-ions; *tert*-butyl groups omitted for clarity. Thermal ellipsoids drawn at the 11% probability level. i = −x, −y, −z. Possible hydrogen bonds in dashed lines. Hydrogen-bonding contacts (Å): N1...O6 2.89 (3), O9...O2 2.81(2), O9...O5 2.84(2), O9...N3 2.72(2).

with bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene[1]. The U-O distances compare well with the U-O^- distances in the complex with bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene (mean value 2.26(1) Å) and in the complexes with *p*-*tert*-butylcalix[8]arene (mean value 2.21(6) Å) and are much lower than the U-OH distances in the last complexes (mean value 2.53(7) Å): this suggests that the four binding oxygen atoms of each calixarene moiety have been deprotonated. The bonding phenolic oxygen atoms are in a plane within ±0.02(1) Å and the uranium atom is at 0.058(1) Å from this mean plane. The O^--U-O^- angles have a mean value of 90(6)°, corresponding to a nearly regular square planar environment around uranyl (octahedral environment around the uranium atom). In the complex with bis(homo-oxa)-*p*-*tert*-butylcalix[4] arene, this environment is more distorted due to the presence of the ether group. The two linear uranyl ions are nearly located on the same axis and the distance between the two facing oxygen atoms O8 and $O8^i$ is 4.06(2) Å.

The conformation of the calixarene is slightly distorted with respect to the usual *pinched cone*: if the torsion angles ϕ and χ as defined by Ugozzoli and Andreetti[9] are considered, two *gauche* angles only, corresponding to bonds with the non-binding phenolic units, differ from the usual values and become *anti* angles. The 4- charge of the dimer is compensated by two protonated triethylamine molecules and two hydronium ions. The triethylammonium ions are at distances from some deprotonated oxygen atoms of the calixarene (O6 and $O6^i$) compatible with the formation of hydrogen bonds: such a situation has already been encountered[1,3,4]. The hydronium ions (O9 and $O9^i$) are located inside the cavity defined by each calixarene: the six O atoms of each calixarene moiety are in a plane within ±0.15(1) Å and the hydronium ions are located at 0.65(1) Å from these mean planes. Short contacts, which suggest the formation of hydrogen bonds, exist between the hydronium ions and two phenolic oxygen atoms non-bonded to the uranyl ion (O2 and O5) and with the nitrogen atom of one acetonitrile molecule (N3) which is included in the hydrophobic cavity of the calixarene. The inclusion of two acetonitrile molecules in free *p*-*tert*-butylcalix[6] arene has previously been described[10]: in both cases, the acetonitrile molecules are out of the pseudo-twofold axis perpendicular to the oxygen atoms mean plane, and tilted with respect to it. Regarding the calixarene moiety itself, the O...O distances are indicative of two possible hydrogen bonds between some protonated and deprotonated oxygen atoms (O1...O2 2.63(2), O4...O5 2.73(2) Å).

This complex provides an example of a rather unusual structure: such a dimerization of two macromolecular units by uranyl ions, which gives rise to a "globular" calixarene dimer encompassing the coordinated metal ions, has not been described previously. A comparison can be made with the complex between thorium(IV) and *p*-*tert*-butylcalix[8]arene reported by Harrowfield *et al.*[2]: in this case, two calixarene units and four metal ions are held together; the main difference with our case is that two thorium ions are included in each calixarene cavity, the two moieties being bridged by some metal-bonded phenolic oxygen atoms and hydroxyl ions, whereas, in our case, the bridging metal ions are equally bonded to each calixarene unit. Recently, some examples have been reported of lanthanide complexes of *p*-sulfonato-calix[5] arene, involving up to four calixarene and metal ions held together *via* sulfonato oxygen atoms[11]. Further work is in progress to characterize other uranium complexes of calixarenes, and particularly inclusion complexes with *p*-*tert*-butyl- and *p*-sulfonato-calixarenes.

EXPERIMENTAL SECTION

Synthesis

The title compound was obtained as a side-product in the course of the investigation of complexes between uranium(IV) and calixarenes. The reaction between UCl_4 (0.5 mmole) and *p*-*tert*-butylcalix[6]arene (0.25 mmole) in presence of triethylamine (5 ml) was carried out in non properly dehydrated and deoxygenated acetonitrile (15 ml) as a solvent, which resulted in an hydrolysis and oxydation of UCl_4 leading to UO_2^{2+} and HCl. A dark brown solution resulted, which was filtered and concentrated under vacuum. Slow cooling of the solution heated at 80°C afforded beautifully shaped red crystals suitable for X-ray crystallography. It should be noted that the acidification of the medium resulting from UCl_4 hydrolysis, and the subsequent formation of hydronium ions, seems to be necessary for this complex to be formed: up to now, we did not manage to obtain it from the direct reaction between *p-tert*-butylcalix[6]arene and uranyl bis(trifluoromethanesulfonate), uranyl nitrate or uranyl chloride, in presence of triethylamine.

Crystal data

$U_2C_{156}H_{216}N_8O_{18}$, $M_r = 2967.56$, monoclinic, $P2_1/n$, $a = 19.183(5)$, $b = 17.726(9)$, $c = 23.206(9)$ Å, $\beta = 106.16(3)°$, $V = 7579(5)$ Å^3, $Z = 2$, $D_c = 1.300$ g.cm^{-3}, $\mu = 20.8$ cm^{-1}.

Structure determination

Data were collected on a capillary-mounted crystal (0.50 × 0.40 × 0.20 mm in size) with an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation (0.71073 Å) in the range $1 < \theta < 20°$, at room temperature, in the $\omega/2\theta$ scan mode. The cell constants were obtained from the least-squares refinement of the setting angles of 25 reflections in the range $8 < \theta < 12°$. 3475 reflections with $I > 3\sigma(I)$, out of 7059 unique reflections measured, were used after Lorentz-polarization correction. Intensity decay (7.3% in 59 hours) was linearly corrected and empirical absorption corrections made (Ψ scans[12]: $T_{min.} = 0.56$, $T_{max.} = 1.00$). Uranium atoms were located from Patterson map interpretation, the remaining atoms from subsequent difference Fourier syntheses. Three out of the six *tert*-butyl groups have been found to be highly disordered and were modelled with six terminal carbon atoms. The solvent molecules have been found and fixed in the last refinement cycles. 414 parameters were refined by full-matrix least-squares on F with anisotropic thermal parameters for uranium and phenolic oxygen atoms; hydrogen atoms were not introduced. Analytical scattering factors for neutral atoms[13] were corrected for the anomalous dispersion components f and f''. The final R values were $R = 0.062$ and $R_w = 0.072$ ($w = 1/\sigma(F)^2$) and the maximum residual density 0.68 e/Å^3. All calculations were performed on a Vax 4200 computer with the Enraf-Nonius MolEN system[14].

REFERENCES

1 Harrowfield, J.M.; Ogden, M.I.; White, A.H. *J. Chem. Soc. Dalton Trans.* **1991**, 979.

2 Harrowfield, J.M.; Ogden, M.I.; White, A.H. *J. Chem. Soc. Dalton Trans.* **1991**, 2625.

3 Thuéry, P.; Keller, N.; Lance, M.; Vigner, J.D.; Nierlich, M. *Acta Cryst.* **1995**, *C51*, 1570.

4 Thuéry, P.; Keller, N.; Lance, M.; Vigner, J.D.; Nierlich, M. *New J. Chem.* **1995**, *19*, 619.

5 Shinkai, S. in 'Calixarenes: a Versatile Class of Macrocyclic Compounds', Vicens, J. and Böhmer, V., Eds., Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; p. 173 and references therein.

6 Guilbaud, P.; Wipff, G. *J. Incl. Phenom.* **1993**, *16*, 169.

7 Johnson, C.K. ORTEPII. Report ORNL-5138, Oak Ridge National Laboratory: Tennessee, USA, 1976.

8 A 3D search using the Cambridge Structural Database (Allen, F.H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31) in its 1994 release containing 146 thousand entries gave about ten compounds with a comparable geometry.

9 Ugozzoli, F.; Andreetti, G.D. *J. Incl. Phenom.* **1992**, *13*, 337.

10 Thuéry, P.; Keller, N.; Lance, M.; Vigner, J.D.; Nierlich, M. *J. Incl. Phenom.* **1995**, *20*, 373.

11 Steed, J.W.; Johnson, C.P.; Barnes, C.L.; Juneja, R.K., Atwood, J.L. to be published in *J. Am. Chem. Soc.*, results presented at the 22nd Course of Crystallography, 'Crystallography of Supramolecular Compounds': Erice, Italy, 1995.

12 North, A.C.T.; Phillips, D.C.; Mathews, F.S. *Acta Cryst.* **1968**, *A24*, 351.

13 International Tables for X-ray Crystallography, Kynoch Press: Birmingham, UK, 1974; Vol. IV.

14 'MolEN: An Interactive Structure Solution Procedure', Enraf-Nonius: Delft, The Netherlands, 1990.