

An unprecedented trigonal coordination geometry for the uranyl ion in its complex with *p*-*tert*-butylhexahomotrioxacalix[3]arene

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Whereas the environment of the uranyl ion in its coordination complexes has always been observed to comprise four, five or six donor atoms close to its equatorial plane, it appears to be pseudo-trigonal, with three oxygen donor atoms only, in the complexes with *p*-*tert*-butylhexahomotrioxacalix[3]arene. This is the lowest coordination number ever observed in a uranyl complex.

The coordination complexes of the uranyl ion UO_2^{2+} have been widely investigated, particularly from the structural point of view. The uranium atom in UO_2^{2+} has never been observed to accommodate a coordination number lower than six.¹ The linear geometry of UO_2^{2+} further limits the coordination geometry to a quasi-planar equatorial one. Among the 470 uranyl complexes present in the 1999 release of the Cambridge Structural Database System,² the majority (60.7%) possess a more or less distorted pentagonal equatorial environment, the hexagonal one is less frequent (33.3%) and always requires at least one chelating ligand and the square one is somewhat rare (6%, excluding the anions $\text{UO}_2\text{Cl}_4^{2-}$ and $\text{UO}_2\text{Br}_4^{2-}$). The complexes of uranyl ions with calixarenes described up to now, in which the cation is encapsulated by the garland of phenolic oxygen atoms of the macrocycle, do not follow this trend since the equatorial four-coordination^{3a,f,h} is as frequent as the five-coordination^{3b,c,e,h} (two other uranyl-calixarene complexes correspond to the former case, but with external uranyl coordination^{3d,g}). There is no example of six-coordination, presumably because calixarenes are not sufficiently small-bite ligands for it to be attained. This deviation from the usual tendency when the uranyl ion is complexed in the calixarene lower rim probably originates from a macrocyclic effect, the four or five oxygen donor atoms being held in a convenient geometry, without much distortion of the free calixarene conformation.^{3a,b,c,e,f} In order to extend our investigation of uranyl complexes beyond the usual calixarenes, we turned to the related ligand *p*-*tert*-butylhexahomotrioxacalix[3]arene (Chart 1), which has been the subject of some structural work in the last years, as well as its derivatives and complexes.⁴

By using two different basic agents, triethylamine and 1,4-diazabicyclo[2.2.2]octane (DABCO), we obtained two iso-

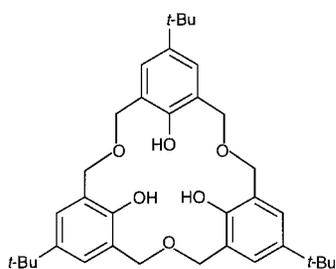


Chart 1 *p*-*tert*-Butylhexahomotrioxacalix[3]arene, H_3L .

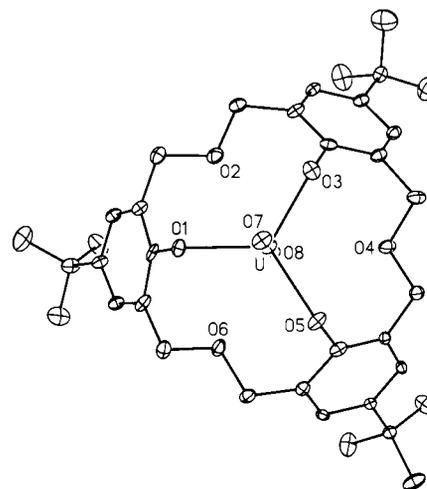


Fig. 1 View of complex **1** showing the pseudo-trigonal environment of the uranyl ion. Hydrogen atoms, solvent and counter-ion omitted for clarity. Selected distances (Å) and angles (°) (values between square brackets are relative to complex **2**): U–O(1) 2.222(11) [2.215(9)], U–O(3) 2.152(8) [2.221(9)], U–O(5) 2.202(10) [2.216(8)], U–O(7) 1.781(10) [1.794(9)], U–O(8) 1.787(8) [1.780(6)]; O(1)–U–O(3) 120.4(5) [112.8(3)], O(3)–U–O(5) 116.6(5) [121.5(3)], O(5)–U–O(1) 120.8(5) [121.9(3)], O(7)–U–O(8) 178.9(5) [179.5(4)].

morphous complexes differing by the counter-ion and solvent molecules: $[(\text{UO}_2^{2+})(\text{L}^{3-})(\text{HNET}_3^+)] \cdot 3\text{H}_2\text{O}$ **1** and $[(\text{UO}_2^{2+})(\text{L}^{3-})(\text{HDABCO}^+)] \cdot 3\text{CH}_3\text{OH}$ **2**, in which H_3L stands for *p*-*tert*-butylhexahomotrioxacalix[3]arene, the structures of which have been determined.[†] The complex core is similar in **1** and **2** and the following discussion applies to both of them. As illustrated in Figs. 1 and 2 in the case of **1**, the complex molecule, which has no crystallographically imposed symmetry, presents a pseudo-trigonal axis. The uranyl ion, located along this axis, is at the centre of the lower rim and is bonded in its equatorial plane to the three deprotonated phenolic oxygen atoms with a mean U–O distance of 2.20(3) Å (both compounds included). This distance compares well with those obtained in other calixarene complexes with aryloxide oxygen atoms³ and is close to the ideal value.³ⁱ The three ether oxygen atoms are at distances from uranium ranging from 3.068(10) to 3.158(10) and from 2.945(9) to 3.280(9) Å in **1** and **2**, respectively [mean value 3.1(1) Å], which precludes any clear-cut coordination bonding. Furthermore, they are located far from the uranyl equatorial plane (distance between the two mean planes, which are not perfectly parallel to each other: about 1.4 Å in both compounds). The uranyl ion is slightly displaced (by 0.186(4) and 0.248(3) Å in **1** and **2**, respectively) out of the plane defined by the three bonding oxygen atoms, towards the plane defined by the three non-bonding ones, which could indicate some kind of

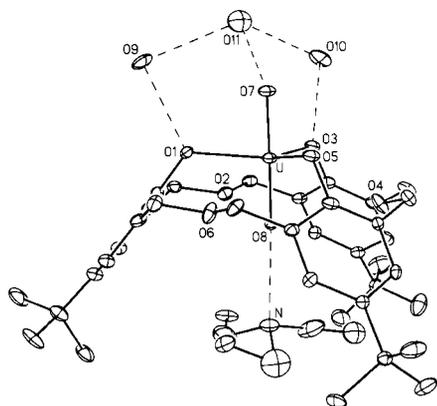


Fig. 2 View of complex **1** including solvent and counter-ion. Hydrogen atoms omitted. Hydrogen bonds in dashed lines. Selected distances (Å): O(1)···O(9) 2.800(11), O(3)···O(10) 2.921(12), O(7)···O(11) 2.916(10), N···O(8) 2.748(10), O(9)···O(11) 3.109(12), O(10)···O(11) 2.820(12). Selected distances (Å) in complex **2**, involving the three methanol molecules and HDABCO⁺ counter-ion: O(1)···O(9) 2.862(9), O(3)···O(10) 2.822(9), O(5)···O(11) 2.701(10), O(7)···O(11) 2.813(8), O(11)···N(2') 2.671(10), with primed atom corresponding to the symmetry operation $x, 1.5 - y, z - 0.5$.

electrostatic interaction between these ether oxygen atoms and the positively charged uranium atom. In the related structure of the uranyl complex of *p-tert*-butyldihomooxalix[4]arene, the cation is also bonded to the four phenolic oxygen atoms, with a mean U–O distance slightly larger than in the present case [2.26(1) Å], and not to the ether oxygen atom, which is at a distance of 3.534(8) Å, with its lone pairs oriented away from uranium.^{3a} The low affinity of uranyl for ether oxygen atoms has already been noticed in the case of crown ether complexes.^{3c} The coordination environment of the uranyl ion in **1** and **2** is genuinely pseudo-trigonal (and that of uranium trigonal bipyramidal), which is the first occurrence of such a low coordination number reported so far. This unusual coordination geometry, which has never been taken into account for the design of selective macrocyclic 'uranophile' ligands,^{3f} appears to deserve further study in this respect. Complexes **1** and **2** present some common features with the trivalent metal complexes of H₃L reported by Daitch *et al.*:^{4c,d} in the latter cases, the trianionic form of the ligand is also involved and some peculiar coordination numbers (Lu³⁺, Y³⁺) or geometry (La³⁺) are observed. However, these complexes are dimeric in the solid state, with μ -aryloxy bridges, and at least one of the ether oxygen atoms is coordinated.

The calixarene conformation is a *cone* one. It can be characterized by the values of the dihedral angles between the mean plane of the molecule, defined for example by the atoms O(2), O(4) and O(6) and the three aromatic rings. These values, which range from 52.1(5) to 53.5(3)° in **1** and from 48.1(3) to 57.7(2)° in **2** [mean value 52(3)°], are significantly larger than those in the uncomplexed form of H₃L [mean value 37(2)°].^{4a} This is connected with an enlargement of the lower rim oxygen atoms array, with O···O distances of 3.705(11)–3.848(10) and 3.695(9)–3.874(9) Å in **1** and **2**, respectively [mean value 3.80(8) Å], to be compared to 3.03(5) Å in H₃L.

In both compounds **1** and **2**, the counter-ion is included in the calixarene cavity, as previously observed in uranyl-calixarene complexes.^{3a,e,f} The protonated ligand H₃L has been considered to present too shallow a cavity in its uncomplexed form to include organic molecules.^{4a} This is no longer true in the present complexed forms, in which the cavity is deeper, as well as in complexes previously described.^{4c,d} The HNEt₃⁺ counter-ion in **1** is hydrogen bonded to one uranyl oxygen atom, as often observed in uranyl complexes,^{3b,c,e,f} whereas HDABCO⁺ in **2** is positioned in such a way that the N···N axis is nearly parallel to the calixarene mean plane. Three solvent molecules, either water or methanol, are present in the crystal structures of **1** and **2**. Those molecules are hydrogen bonded to the uranyl oxygen atom directed towards the outside

part of the calixarene, with phenolic oxygen atoms and also with HDABCO⁺ in **2**. The water molecules in **1** are also hydrogen bonded one to the other.

Notes and references

† Preparation of *p-tert*-butylhexahomotrioxalix[3]arene (H₃L). H₃L has been synthesized as reported in the literature.⁵ Anal., calc. for C₃₆H₄₈O₆: C, 74.97; H, 8.39; found: C, 74.98; H, 8.37%. Mp 238–239 °C. ¹H-NMR (200 MHz in CDCl₃), ppm from SiMe₄: δ 8.57 (s, 3H, ArOH), 7.12 (s, 6H, ArH), 4.72 (s, 12H, ArCH₂O), 1.23 (s, 27H, *tert*-C₄H₉). Preparation of **1**. An excess of NEt₃ (6 ml) was added to a solution of H₃L (0.5 mmol) in CH₃OH (100 ml). A solution of uranyl nitrate hexahydrate (0.5 mmol) in CH₃OH (30 ml) was then added dropwise, resulting in a bright orange solution which was stirred for two hours at room temperature. Dark orange crystals suitable for X-ray crystallography deposited within 24 hours.

Preparation of **2**. Same preparation as for **1**, an excess of DABCO (4 mmol) being used in place of NEt₃. Light orange crystals suitable for X-ray crystallography deposited within 24 hours. ¹H-NMR after evaporation of the solvents of crystallization (200 MHz in CDCl₃), ppm from SiMe₄: 7.15 (s, 6H, ArH), 5.99 (d, $J = 8.7$ Hz, 6H, AB system, ArCH₂O), 4.41 (d, $J = 8.7$ Hz, 6H, AB system, ArCH₂O), 1.20 (s, 27H, *tert*-C₄H₉), HDABCO⁺ detected as a large singlet at δ 2.73. FAB⁺ MS for both compounds: m/z 845.3 [(UO₂²⁺)(L³⁻) + 2H⁺].

Crystal data for **1**: [(UO₂²⁺)(L³⁻)(HNEt₃⁺)]·3H₂O, C₄₂H₆₇NO₁₁U, $M = 1000.00$, monoclinic, space group $P2_1/c$, $a = 16.464(3)$, $b = 14.203(2)$, $c = 19.590(2)$ Å, $\beta = 91.844(9)^\circ$, $V = 4579(4)$ Å³, $Z = 4$, $D_c = 1.451$ g cm⁻³, $\mu = 3.600$ mm⁻¹, $F(000) = 2024$.

Crystal data for **2**: [(UO₂²⁺)(L³⁻)(HDABCO⁺)]·3CH₃OH, C₄₅H₇₀N₂O₁₁U, $M = 1053.06$, monoclinic, space group $P2_1/c$, $a = 16.481(2)$, $b = 14.2749(15)$, $c = 20.314(2)$ Å, $\beta = 90.020(3)^\circ$, $V = 4779(4)$ Å³, $Z = 4$, $D_c = 1.464$ g cm⁻³, $\mu = 3.453$ mm⁻¹, $F(000) = 2136$. Data collected at 270 K on a Nonius Kappa-CCD area-detector diffractometer with Mo-K α radiation. Absorption effects empirically corrected. Structures solved by direct methods. One *tert*-butyl group disordered in **2**, modelled with nine terminal carbon atoms. Hydrogen atoms included at calculated positions as riding atoms, except those bonded to nitrogen atoms, to water and methanol oxygen atoms and those in the disordered part of **2**. All non-hydrogen atoms refined anisotropically, except the disordered ones in **2**. Refinement by full-matrix least-squares on F^2 . $R_1 = 0.082$ and 0.074 ($wR_2 = 0.172$ and 0.153) for **1** and **2**, respectively. CCDC reference number 186/1615. See <http://www.rsc.org/suppdata/dt/1999/3151/> for crystallographic files in .cif format.

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