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Uranyl ions as supramolecular linkers in a bis(hexahomotrioxacalix[6]arene) hexa-uranate complex

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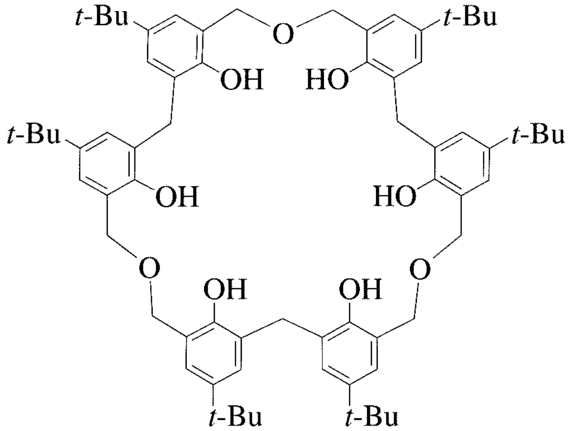
Large calixarenes and homooxacalixarenes provide a unique means of complexing discrete poly-uranate species by phenoxide bonding. In the present case, owing to the particular nature of UO_2^{2+}, which presents both equatorial coordination and axial hydrogen bonding abilities, two homooxacalixarene trinuclear complexes assemble in a self-recognition process to give a hexa-uranate cluster surrounded by two divergent macrocycles.

The structural chemistry of the uranyl ion UO_2^{2+} has recently been enriched by some novel features revealed by the investigation of its complexes with poly-aryloxide ligands in the calixarene and homooxacalixarene families.[1] The most notable results are the first pseudo-trigonal coordination environment for this ion[2] and the possibility of building poly-uranate clusters of unprecedented geometries by using large calixarenes or homooxacalixarenes.[1,3,4] A somewhat little used characteristic of UO_2^{2+} is the Lewis basicity of the oxo ligands, which may result in direct coordination to a second uranium ion[3,5] and even oxo exchange[5] or in the more ubiquitous effect of hydrogen bonding.[6] The latter has been shown to confer a guest-linking role to uranyl ions serving as connectors in a molecular box.[7] UO_2^{2+} may thus be considered as a building block with both equatorial and axial connectivity abilities. The present work was primarily aimed at investigating poly-uranate complexation by a new large homooxacalixarene, *p-tert*-butylhexahomotrioxacalix[6]arene, denoted L (Scheme 1). However, the trinuclear complex formed was serendipitously found to self-assemble owing to complementary hydrogen bonds, giving a hexa-uranate cluster which illustrates the underrated potential of uranyl ions for the design of supramolecular systems.



Scheme 1 *p-tert*-Butylhexahomotrioxacalix[6]arene, L.

Two forms of the complex have been obtained, depending on the solvent used: $[HDABCO]_3[(UO_2)_3(L-6H)(OH)_3]\cdot(HDABCO)\cdot(NO_3)\cdot2.5CHCl_3\cdot3.5CH_3OH$ **1**, and $[(HDABCO)_2(DABCO–CH_2Cl)][(UO_2)_3(L-6H)(OH)_3]\cdot(DABCO)\cdot4CH_3CN\cdot2CH_3OH$ **2**, with chloroform and methylene chloride as solvents, respectively, and their crystal structures have been determined.† The anionic complex core $[(UO_2)_3(L-6H)(OH)_3]^{3-}$ is identical in both cases, the main difference arising in **2** from the previously documented chloroalkylation of the basic agent 1,4-diazabicyclo[2.2.2]octane (DABCO) by methylene chloride[8] and subsequent inclusion in the calixarene cavity of the reaction product 1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane, $DABCO–CH_2Cl^+$. As illustrated in Fig. 1 in the case of

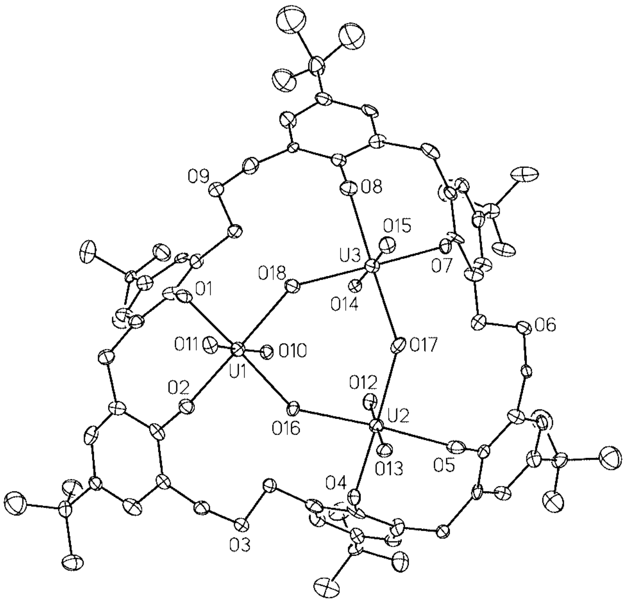


Fig. 1 View of the anionic complex core $[(UO_2)_3(L-6H)(OH)_3]^{3-}$ in **1**. Hydrogen atoms, solvents and counter-ions omitted for clarity. Ellipsoids drawn at the 20% probability level. Selected distances (Å) and angles (°) (values in square brackets are relative to complex **2**): U(1)–O(1) 2.213(12) [2.193(11)], U(1)–O(2) 2.163(13) [2.247(11)], U(1)–O(10) 1.799(12) [1.789(9)], U(1)–O(11) 1.827(11) [1.803(9)], U(1)–O(16) 2.305(12) [2.324(11)], U(1)–O(18) 2.346(13) [2.356(10)], U(2)–O(4) 2.199(12) [2.221(11)], U(2)–O(5) 2.242(15) [2.232(9)], U(2)–O(12) 1.785(14) [1.774(9)], U(2)–O(13) 1.779(14) [1.789(9)], U(2)–O(16) 2.350(12) [2.349(10)], U(2)–O(17) 2.325(13) [2.348(10)], U(3)–O(7) 2.205(12) [2.201(11)], U(3)–O(8) 2.251(13) [2.212(11)], U(3)–O(14) 1.807(14) [1.774(9)], U(3)–O(15) 1.807(14) [1.801(10)], U(3)–O(17) 2.340(12) [2.313(10)], U(3)–O(18) 2.287(14) [2.324(10)]; O(10)–U(1)–O(11) 176.3(5) [179.1(5)], O(12)–U(2)–O(13) 178.9(6) [179.0(5)], O(14)–U(3)–O(15) 177.4(6) [179.9(5)], U(1)–O(16)–U(2) 134.5(6) [135.3(4)], U(2)–O(17)–U(3) 136.7(5) [136.2(4)], U(1)–O(18)–U(3) 135.9(6) [136.3(4)].

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complex **1**, the molecule presents a pseudo-trigonal axis. The macrocycle includes three uranyl ions bridged by three oxygen atoms, which can be ascribed to hydroxide ions on the basis of charge equilibrium and geometric considerations (it must be noted that water is present during the reaction). Each uranium atom is bound to the two *trans* apical oxo atoms [mean U=O bond length 1.79(2) Å, including both compounds, as for all the mean values that follow], two phenoxide oxygen atoms in *cis* positions [mean U–O bond length 2.22(3) Å] and two hydroxide ions [mean U–O bond length 2.33(2) Å], resulting in a pseudo-octahedral (with tetragonal compression) coordination of uranium. The planes defined by the four equatorial donors for each uranium atom (rms deviation 0.029–0.165 Å), which also contain the metal atom, intersect with dihedral angles in the range 33.6(2)–36.8(2)° [mean value 35(1)°]. The three ether oxygen atoms are clearly non-bonding, their lone pairs being directed away from the macrocycle centre [mean U ··· O distance with the closer uranium atoms 5.0(2) Å; mean distance to the phenoxide O_6 mean plane 1.1(1) Å]. The calixarene is in a much distorted *cone* conformation, with aromatic rings more or less tilted with respect to the macrocycle mean plane, in an alternate fashion [mean values of dihedral angles with the phenoxide O_6 mean plane 46(12) and 72(3)° for the two categories, respectively]. The 3− charge of the complex core $[(UO_2)_3(L - 6H)(OH)_3]$ is compensated by three HDABCO/DABCO–CH_2Cl cations. In both compounds, two of the HDABCO cations are located out of the calixarene cavity and hydrogen bound to phenoxide oxygen atoms [mean N ··· O distance 2.8(1) Å], the last counter-ions being included in the cavity (with possible hydrogen bonding to the three oxo groups in **1**). A fourth HDABCO moiety in **1** is involved in hydrogen bonding to a nitrate ion, which is otherwise non-bonding. As previously stated,[4] the size of L can be characterized by the sum of the numbers of phenolic and ether groups, which amounts to 9. This is roughly equivalent to the size of *p*-*tert*-butylcalix[9]arene, which has been shown to be able to complex two uranyl ions while keeping a free triphenolic unit,[1] potentially making it a trinuclear-complexing species. The present result confirms the relative ease with which a poly-uranate cluster of desired nuclearity can be obtained by calixarene/homooxacalixarene complexation.

The most original feature in both **1** and **2** is the assembling of two $[(UO_2)_3(L - 6H)(OH)_3]^{3-}$ units to give a hydrogen bound supramolecular system. The three unshielded uranyl oxo groups directed towards the exterior of the molecule are involved in hydrogen bonding to the three hydroxide ions of a neighbouring, centrosymmetrically related, molecule, and *vice versa* (Fig. 2), in what may be called a self-recognition process. The resulting assembly, with two divergent complexes held by six hydrogen bonds [mean OH ··· O(oxo) distance 2.79(5) Å], assumes an approximate S_3 symmetry, the uranium atoms being at the corners of a trigonal antiprism (Fig. 3). Not only the geometry of the trinuclear unit is unprecedented in discrete poly-uranate complexes,[9] but, as far as we know, the self-complementarity of two such units in terms of hydrogen bonding donor and acceptor site location has never been observed in uranyl coordination chemistry. However, an (OH) ··· O(oxo) hydrogen bonding pattern is observed between adjacent layers in uranyl dihydroxide,[10] but with a different, hexagonal bipyramidal, coordination environment, in which six μ_3-hydroxide ions surround UO_2^{2+}, with the consequence of longer U–O(hydroxide) bond lengths (mean value 2.48(3) Å):[11] it appears quite remarkable to find in the present discrete cluster a similar arrangement, which may thus be considered a robust feature usable in the design of novel supramolecular systems. Recently, some approaches aimed at combining coordination and hydrogen bonds, which are among the widest used interactions in supramolecular chemistry, have been developed.[12] UO_2^{2+} appears to unite in itself both a directed coordination bonding scheme in its equatorial plane and an axial hydrogen bond-acceptor ability. The possibility of using the latter to extend the structure into a 3-D assembly or as a functional component of the system[7] justify a reappraisal of this ion as a supramolecular component.

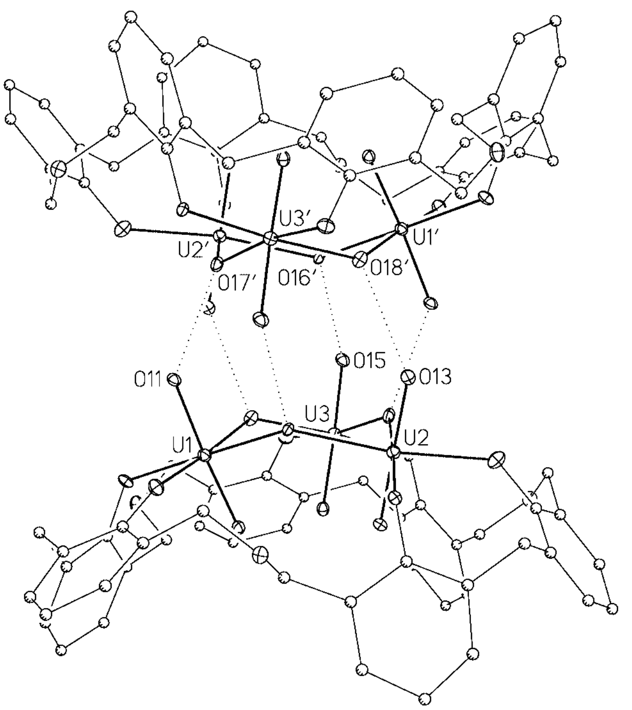

Fig. 2 View of the hexanuclear assembly built by hydrogen bonding from two $[(UO_2)_3(L - 6H)(OH)_3]^{3-}$ units in **1**. *tert*-Butyl groups, hydrogen atoms, solvents and counter-ions omitted for clarity. The carbon atoms are represented as small spheres of arbitrary radii. Primed atoms are related to their unprimed counterpart by the symmetry centre. Hydrogen bonds as dotted lines. Ellipsoids drawn at the 10% probability level. Selected distances (Å) (values in square brackets are relative to complex **2**): O(11) ··· O(17′) 2.726(16) [2.778(13)], O(13) ··· O(18′) 2.85(2) [2.850(12)], O(15) ··· O(16′) 2.764(19) [2.776(13)].

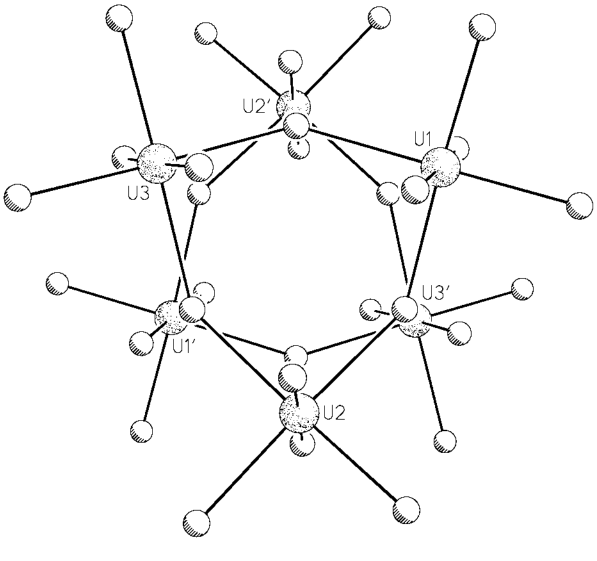

Fig. 3 View of the hexa-uranate cluster along the pseudo-S_3 axis. Uranium and oxygen atoms only are represented. Primed atoms are related to their unprimed counterpart by the symmetry centre.

Notes and references

† Preparation of *p*-*tert*-butylhexahomotrioxacalix[6]arene (L). L has been synthesized as reported elsewhere.[13] Anal., calc. for $C_{69}H_{90}O_9$: C, 77.93; H, 8.53; found: C, 77.76; H, 8.84%. ^{1}H-NMR (200 MHz, $CDCl_3$, referenced to $SiMe_4$): δ 1.25 (s, 54H, *t*-Bu), 4.12 (s, 6H, ArC*H*$_2$Ar), 4.61 (s, 12H, C*H*$_2$OC*H*$_2$), 6.93 (d, *J* = 2.0 Hz, 6H, Ar*H*), 7.27 (d, *J* = 2.0 Hz, 6H, Ar′*H*), 8.74 (s, 6H, ArO*H*).

Preparation of **1**. A large excess of 1,4-diazabicyclo[2.2.2]octane (DABCO) (3 mmol) was added to a solution of L (15 mg, 0.014 mmol) in $CHCl_3$ (100 ml). A solution of uranyl nitrate hexahydrate in excess (100 mg, 0.2 mmol) in CH_3CN (30 ml) was then added dropwise, resulting in a pale orange solution which was refluxed for one hour. Dark orange crystals of rather low quality but suitable for X-ray crystallography deposited within 24 hours upon recrystallization from $CHCl_3$–CH_3OH (1 : 1). No NMR was performed, the compound being insoluble in $(CH_3)_2CO$, $CHCl_3$, DMF and THF. The spectrum of the uncomplexed ligand is obtained in $CDCl_3$–(dmso-d6), which indicates that decomplexation seemingly occurs in dmso. FAB-MS: *m*/*z* 3733.1 corresponding to $[(UO_2)_6(L - 6H)_2]$; some peaks attributable to polyuranate aggregates are also observed: 1922.3 $[(UO_2)_7O_2]$, 1652.3 $[(UO_2)_6O_2]$, 1382.2 $[(UO_2)_5O_2]$, 1096.2 $[(UO_2)_4O]$ and 826.1 $[(UO_2)_3O]$.

Preparation of **2**. Same preparation as for **1**, with CH_2Cl_2 in place of $CHCl_3$. Dark orange crystals of rather low quality but suitable for X-ray crystallography deposited within 24 hours.

Crystal data for **1**: $[HDABCO]_3[(UO_2)_3(L - 6H)(OH)_3]\cdot(HDABCO)\cdot(NO_3)\cdot2.5CHCl_3\cdot3.5CH_3OH$, $C_{99}H_{155.5}Cl_{7.5}N_9O_{24.5}U_3$, $M = 2843.79$, monoclinic, space group $P2_1/c$, $a = 20.301(2)$, $b = 30.908(2)$, $c = 19.427(2)$ Å, $\beta = 103.992(3)°$, $V = 11828(2)$ Å^3, $Z = 4$, $D_c = 1.597$ g cm^{-3}, $\mu = 4.335$ mm^{-1}, $F(000) = 5648$.

Crystal data for **2**: $[(HDABCO)_2(DABCO–CH_2Cl)][(UO_2)_3(L - 6H)(OH)_3]\cdot(DABCO)\cdot4CH_3CN\cdot2CH_3OH$, $C_{104}H_{159}ClN_{12}O_{20}U_3$, $M = 2646.97$, triclinic, space group $P\bar{1}$, $a = 18.162(2)$, $b = 18.970(2)$, $c = 21.0020(14)$ Å, $\alpha = 80.992(7)$, $\beta = 85.442(7)$, $\gamma = 61.773(4)°$, $V = 6296.5(10)$ Å^3, $Z = 2$, $D_c = 1.396$ g cm^{-3}, $\mu = 3.931$ mm^{-1}, $F(000) = 2640$.

Data collected at 100 K on a Nonius Kappa-CCD area detector diffractometer using graphite monochromated Mo-Kα radiation (λ 0.71073 Å). Absorption effects empirically corrected. Structures solved by direct methods. Disorder on some solvent molecules in both compounds and on three *tert*-butyl groups in **2**. Eight small voids in **1** (4 × 71 and 4 × 22 Å^3) and four larger ones in **2** (4 × 267 Å^3) may indicate the presence of disordered and possibly low-occupancy, unresolved solvent molecules. Hydrogen atoms included at calculated positions as riding atoms, except those bound to oxygen and nitrogen atoms and those of disordered fragments and solvent molecules. All non-hydrogen atoms refined anisotropically, with restraints on bond lengths and displacement parameters in several *tert*-butyl groups, DABCO and solvent molecules. Refinement by full-matrix least-squares on F^2. $R1 = 0.082$ and 0.081 ($wR2 = 0.127$ and 0.165) for **1** and **2**, respectively. CCDC reference numbers 162718 and 162719. See http://www.rsc.org./suppdata/dt/b1/b109451n/ for crystallographic data in CIF or other electronic format.

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11 (OH) ··· O(oxo) hydrogen bonding leading to an extended network, but devoid of the self-complementary aspect displayed in the present compounds, has recently been described in uranyl hydroxide species obtained under highly alkaline aqueous conditions: D. L. Clark, S. D. Conradson, R. J. Donohoe, D. Webster Keogh, D. E. Morris, P. D. Palmer, R. D. Rogers and C. D. Tait, *Inorg. Chem.*, 1999, **38**, 1456. The use of large calixarenes as ligands may enable the study of discrete hydroxy-bridged poly-uranate species in a basic medium by preventing the formation of insoluble uranate salts.

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