

Complexation of a hexameric uranium(VI) cluster by *p*-benzylcalix[7]arene

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The reaction of uranyl nitrate hexahydrate with *p*-benzylcalix[7]arene (H_7L) in the presence of 1,4-diazabicyclo-[2.2.2]octane (DABCO) resulted in the formation of the compound $(UO_2^{2+})_6(L^{7-})_2(O^{2-})_2(HDABCO^+)_6 \cdot 3CH_3CN \cdot CHCl_3 \cdot 5CH_3OH \cdot 3H_2O$ **1**, whose crystal structure has been determined. In the symmetry-centred complex core a hexanuclear uranium(VI) cluster is surrounded by two calixarene units. Each calixarene, in a conformation different from the usual one, encompasses two UO_2^{2+} moieties, which are bonded to three or four phenolic oxygen atoms and also one to the other by one of their oxygen atoms. The two other UO_2^{2+} ions are located between the two calixarene moieties and are involved, together with one of the former ions, in two pseudo-trigonal μ_3 -oxo-centred assemblies. This complex, which represents one of the largest metal ion assemblies in calixarene chemistry, illustrates the 'cluster keeper' character of the larger calixarenes.

The discovery by Shinkai *et al.*¹ that some calixarene derivatives behave as 'uranophiles' has attracted much interest for the last ten years, but has left open the question of the structures of the complexes formed. The first examples of fully characterized actinide complexes of calixarenes were later provided by Harrowfield *et al.*, who reported the synthesis and crystal structures of the uranyl complex of bis(homo-oxa)-*p*-tert-butylcalix[4]arene² and of the tetranuclear thorium complex of *p*-tert-butylcalix[8]arene.³ The former compound demonstrates that simple calixarenes, in a basic medium, are able to provide the equatorial environment (here, four-co-ordinate, but more frequently five-co-ordinate) suitable for uranyl ions. We further extended this work by describing the crystal structures of the uranyl complexes of *p*-tert-butylcalix[*n*]arenes, with *n* = 5–8.^{4–7} With *n* = 5⁶ and 7,⁷ as in the case of bis(homo-oxa)-*p*-tert-butylcalix[4]arene, the complexes are mononuclear, the uranyl ion being in an irregular pentagonal (*n* = 5) or square-planar (*n* = 7) equatorial environment. In the latter case the four oxygen atoms of the tetrameric subunit of the calixarene only are linked to the metal ion. In both cases, the conformation of the complexed calixarene appears very close to that of the uncomplexed one. With *n* = 8⁴ the calixarene is large enough to accommodate two uranyl ions, each of them in a pentagonal equatorial environment made of four phenolic oxygen atoms and one bridging hydroxyl ion. The case *n* = 6 is peculiar since the only complex we obtained was a dimeric species in which each calixarene acts as a bidentate ligand towards each uranyl ion, the uranyl axes being parallel to the calixarene mean plane.⁵ In all the cases the complexes were obtained with triethylamine as a deprotonating agent. Two other studies worthy of note were reported recently: the first deals with the extraction properties of a 1-acid-3-diethylamide substituted calix[4]arene and the crystal structure of its dimeric uranyl complex, in which the 'lower rim' substituents provide three of the binding sites, two uranyl ions being 'sandwiched' between two calixarene moieties;⁸ the other demonstrates the role of caesium ions in uranyl complexation by *p*-tert-butylcalix[6]arene.⁹

All the results published before 1997 and some other unpublished ones have been reviewed by Harrowfield, with a particular emphasis on ring-size effects.¹⁰ Among the results

discussed in this review but not yet published in detail, some present a particular relevance to the results reported herein. Two *p*-tert-butylcalix[*n*]arenes give trinuclear uranyl complexes. With *n* = 6 the complex is oxo-centred, each of the three calixarenes being bidentate.¹¹ With *n* = 8 the complex possesses a core similar to that of the dinuclear complex already reported, with a third uranyl ion bonded to one oxygen atom from each of the two former ions; the obtention of this new complex results from the replacement of triethylammonium by tetramethylammonium as counter ion.¹² A dinuclear complex is also obtained in the case *n* = 9,¹³ which is reminiscent of the dinuclear complex obtained with the acyclic analogue of *p*-tert-butylcalix[6]arene.¹⁴ One conclusion of this review is that the larger calixarenes might be regarded as receptors for uranate clusters rather than for the uranyl ion itself. The same trend is illustrated by the thorium complex of *p*-tert-butylcalix[8]arene, which is described as a 'hydroxothorium oligomer complex',³ and by rare-earth-metal complexes, with the occurrence of oxometal clusters for the largest calixarenes.¹³ The expression 'cluster keeper' was coined by Harrowfield to qualify these large calixarenes.

The difficulties encountered in growing single crystals in this family of compounds led us to investigate basic agents other than triethylamine. We turned to DABCO (1,4-diazabicyclo-[2.2.2]octane) which we thought to be able to facilitate crystallization, owing to its quasi-spherical shape. We report in this paper the synthesis and crystal structure of the hexanuclear uranyl complex of *p*-benzylcalix[7]arene, which never crystallized in the presence of triethylamine. This is one of the highest nuclearity complexes of a calixarene to date, which confirms the trends stated before.

Experimental

Synthesis

***p*-Benzylcalix[7]arene.** The reaction was conducted according to a procedure previously described.¹⁵ *p*-Benzylphenol (9.21 g, 50 mmol), paraformaldehyde (5.00 g, 160 mmol) and 14 M KOH (0.5 ml), dispersed in tetraline (80 ml), were heated at

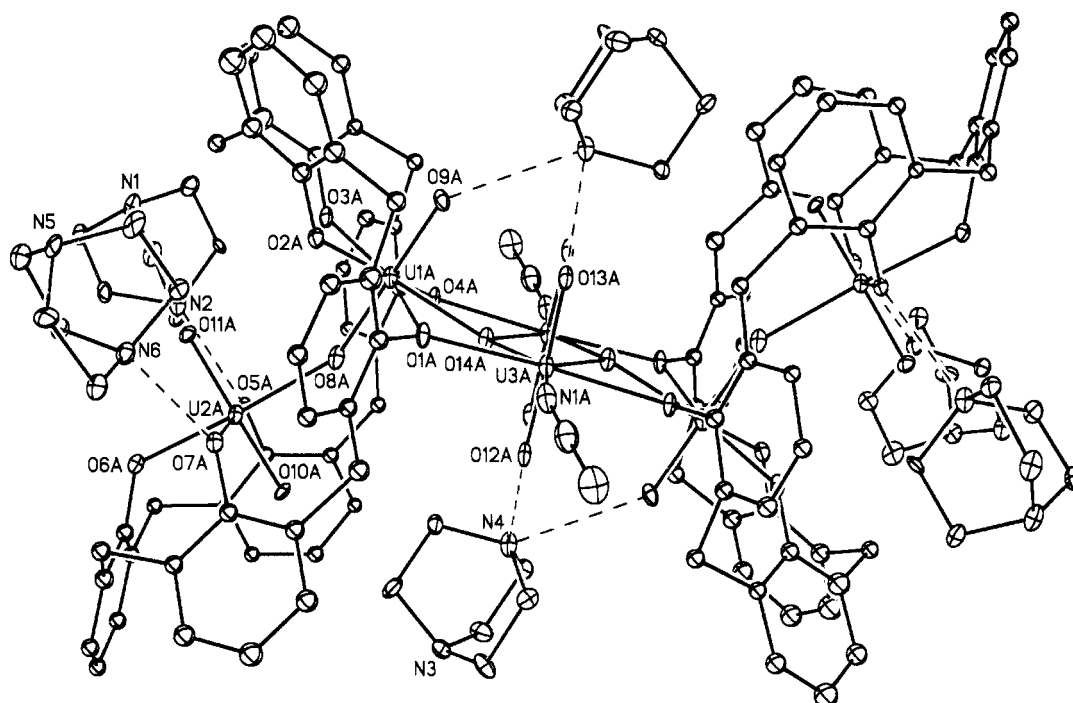


Fig. 1 View of molecule A in complex 1. Hydrogen atoms, *p*-benzyl substituents and solvent molecules omitted for clarity.

180–185 °C under a nitrogen atmosphere for 5 h, in a 250 ml round-bottomed flask equipped with a Dean–Stark collector. After evaporation of tetraline under reduced pressure (10^{-3} mmHg), the resulting brown solid was dispersed in CHCl_3 in which 1 M HCl was added. The biphasic mixture was magnetically stirred during 3 h. Then the organic layer was washed twice with water and dried over MgSO_4 . After filtration, the solvents were removed to yield a brown-yellow residue which precipitated on addition of acetone. A white solid (0.350 g) was filtered off by suction and shown to be pure *p*-benzylcalix[8]arene by comparison with a previous sample¹⁵ (yield 3%). Then the filtrate was evaporated and the residue triturated with acetone. After 2 h a precipitate was formed and filtered off to give a white solid identified as *p*-benzylcalix[5]arene (0.220 g) by comparison with a previous sample¹⁵ (yield 1%). Once again the filtrate was evaporated and precipitated with acetone. After 6 h the precipitate was filtered off by suction to yield *p*-benzylcalix[7]arene (2.15 g, yield 16%, mp >300 °C. ^1H NMR (CDCl_3 , from TMS): δ 10.33 (s, 1 H, aryl OH); 7.32–7.11 (m, 5 H, phenyl); 6.94 (s, 1 H, aromatic); 6.90 (s, 1 H, aromatic); 3.86 (s, 2 H, CH_2); and 3.84 (s, 2 H, CH_2). FAB⁺ MS: m/z 1372.6. Calc. for $\text{C}_{14}\text{H}_{12}\text{O}$: C, 85.68; H, 6.16. Found: C, 85.70; H, 6.43%.

Uranyl complex 1. *p*-Benzylcalix[7]arene (300 mg, ≈ 0.22 mmol) was dissolved in CHCl_3 (100 ml) and an excess of 1,4-diazabicyclo[2.2.2]octane (DABCO, 470 mg, ≈ 4 mmol) added. A solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (370 mg, ≈ 0.7 mmol) in CH_3CN (40 ml) was then added dropwise, yielding a dark brownish solution that became dark red upon reflux. The resulting product was recrystallized from CHCl_3 – CH_3OH (1 : 1), giving dark red crystals suitable for X-ray crystallography. The crystals were unstable and decomposed rapidly, even in their mother-solution. ^1H NMR (CDCl_3 , from TMS): three multiplets could be detected which were not assigned, δ 7.33–6.85 (m); 4.10–3.62 (m); 2.70–1.95 (m). FAB⁺ MS: m/z 4318.2 [$(\text{UO}_2^{2+})_6(\text{C}_{98}\text{H}_{84}\text{O}_7)_2 - \text{H}$].

Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer¹⁶ using graphite monochromated Mo- $\text{K}\alpha$ radiation (0.71073 Å). The crystal was introduced in a Lindemann

glass capillary with a protecting ‘Paratone’ oil (Exxon Chemical Ltd.) coating. The data were processed with the HKL package.¹⁷ The structure was solved by direct methods with SHELXS 86¹⁸ and subsequent Fourier-difference synthesis and refined by full-matrix least squares on F^2 with SHELXL 93.¹⁹ Absorption effects were corrected empirically with the program MULABS from PLATON.²⁰ All the aromatic rings were refined as idealized hexagons. One of the benzyl groups in molecule B is disordered, the aromatic ring being distributed over two positions sharing two lateral carbon atoms, with occupancies refined to 0.69(4) and 0.31(4). Owing to low crystal quality and large number of atoms, some restraints or constraints had to be applied on bond length and displacement parameters, particularly in the solvent molecules. The methanol molecules appeared badly on the Fourier-difference maps and the presence of other highly disordered solvent molecules cannot be ruled out. Uranium, oxygen, nitrogen and chlorine atoms were refined anisotropically, as well as the carbon atoms of the acetonitrile and DABCO moieties. The hydrogen atoms were introduced at calculated positions (except those bonded to nitrogen atoms in DABCO, those of water and chloroform molecules and those in the disordered benzyl group) as riding atoms with a displacement parameter equal to 1.2 (CH , CH_2) or 1.5 (CH_3) times that of the parent atom. The nine first peaks in the final Fourier-difference map are located near uranium atoms as a result of residual absorption effects; the other peaks are lower than $1 \text{ e } \text{\AA}^{-3}$. Crystal data and structure refinement parameters are given in Table 1. The molecular drawings were done with SHELXTL.²¹ All calculations were performed on a Silicon Graphics R10000 workstation.

CCDC reference number 186/1493.

See <http://www.rsc.org/suppdata/dt/1999/2589/> for crystallographic files in .cif format.

Results and discussion

The triclinic cell contains two independent and differently oriented dimeric molecules, each with a crystallographically imposed symmetry centre and consequently the asymmetric unit is composed of two half-molecules. The chemical formula of one complete unit deduced from the crystallographic investigation is $(\text{UO}_2^{2+})_6(\text{L}^{7-})_2(\text{O}^{2-})_2(\text{HDABCO}^+)_6 \cdot 3\text{CH}_3\text{CN} \cdot \text{CHCl}_3 \cdot$

5CH₃OH·3H₂O, where H₇L is *p*-benzylcalix[7]arene. One of the two molecules (A) is presented in Fig. 1; the second molecule (B) is analogous to A in its overall shape and the following discussion applies to both of them. Selected distances and angles are given in Table 2. The two symmetry-related calixarene moieties face each other, each containing two UO₂²⁺ ions, one of them [U(1)] much more inclined than the other one [U(2)] towards the calixarene mean plane. The two remaining UO₂²⁺ ions [U(3), U(3')] are located between the two calixarene cores (primed atoms are related to unprimed ones by the symmetry centre). Each type of UO₂²⁺ ion possesses a different

environment, as illustrated in Fig. 2. Atom U(1) is bonded to four calixarene phenolic oxygen atoms which separate into two groups, the first one [O(2), O(3)] corresponding to distances ranging from 2.18(2) to 2.21(2) Å close to

Table 1 Crystal data and structure refinement details

Empirical formula	C ₂₄₄ H ₂₆₈ Cl ₃ N ₁₅ O ₃₆ U ₆
<i>M</i>	5521.26
<i>T</i> /K	123(2)
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	19.969(2)
<i>b</i> /Å	20.071(2)
<i>c</i> /Å	30.876(3)
<i>a</i> /°	82.306(5)
<i>β</i> /°	79.979(4)
<i>γ</i> /°	87.709(5)
<i>V</i> /Å ³	12074(3)
<i>Z</i>	2
<i>μ</i> /mm ^{−1}	4.112
Reflections collected	49631
Independent reflections	26917
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	12634
<i>R</i> _{int}	0.10
Number of parameters	1433
<i>R</i> 1	0.091
<i>wR</i> 2	0.206

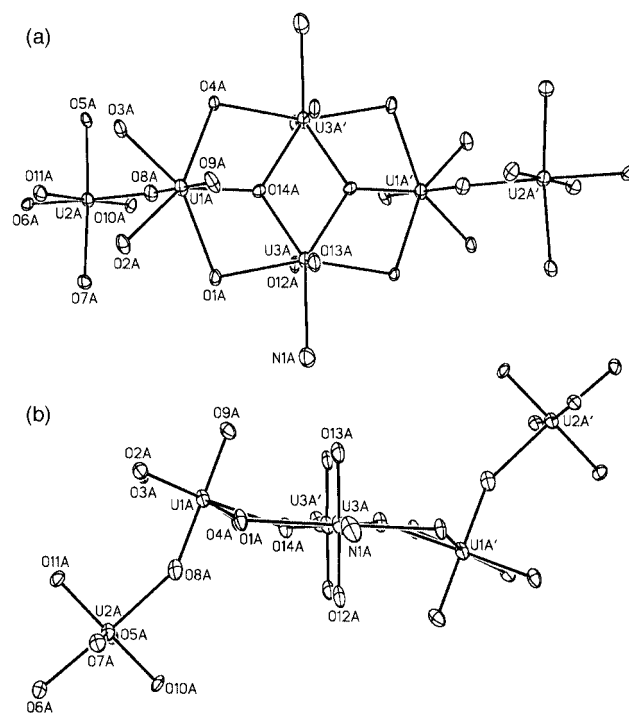


Fig. 2 Two views of the (UO₂²⁺)₆ cluster and its environment (molecule A).

Table 2 Selected bond distances (Å) and angles (°). Primed atoms are related to unprimed ones by the molecule symmetry centre

Uranium environment			
U(1A)–O(1A)	2.51(2)	U(2A)–O(5A)	2.28(2)
U(1A)–O(2A)	2.19(2)	U(2A)–O(6A)	2.22(2)
U(1A)–O(3A)	2.21(2)	U(2A)–O(7A)	2.28(2)
U(1A)–O(4A)	2.49(2)	U(2A)–O(8A)	2.30(2)
U(1A)–O(8A)	1.90(2)	U(2A)–O(10A)	1.78(2)
U(1A)–O(9A)	1.82(2)	U(2A)–O(11A)	1.83(2)
U(1A)–O(14A)	2.20(2)	U(1A)···U(3A)	3.830(2)
U(1A)···U(2A)	4.096(2)	U(1A)···U(3A')	3.844(2)
U(3A)···U(3A')	3.707(2)		
U(1B)–O(1B)	2.53(2)	U(2B)–O(5B)	2.26(2)
U(1B)–O(2B)	2.18(2)	U(2B)–O(6B)	2.12(3)
U(1B)–O(3B)	2.19(2)	U(2B)–O(7B)	2.27(2)
U(1B)–O(4B)	2.54(2)	U(2B)–O(8B)	2.35(2)
U(1B)–O(8B)	1.86(2)	U(2B)–O(10B)	1.77(1)
U(1B)–O(9B)	1.81(2)	U(2B)–O(11B)	1.76(2)
U(1B)–O(14B)	2.12(2)	U(1B)···U(3B)	3.832(2)
U(1B)···U(2B)	4.085(2)		
U(3B)···U(3B')	3.726(2)		
O(8A)–U(1A)–O(9A)	179.2(8)	O(8B)–U(1B)–O(9B)	179.0(8)
O(10A)–U(2A)–O(11A)	179.2(9)	O(10B)–U(2B)–O(11B)	179.5(9)
O(12A)–U(3A)–O(13A)	173.9(9)	O(12B)–U(3B)–O(13B)	174.2(8)
O···O distances in calixarenes			
O(1A)···O(2A)	2.79(3)	O(2A)···O(3A)	2.89(3)
O(4A)···O(5A)	4.50(3)	O(5A)···O(6A)	3.05(3)
O(7A)···O(1A)	4.45(3)	O(2B)···O(3B)	2.83(3)
O(1B)···O(2B)	2.87(3)	O(5B)···O(6B)	2.93(3)
O(4B)···O(5B)	4.55(3)		
O(7B)···O(1B)	4.54(3)		
Hydrogen bonds			
N(2)···O(5A)	2.62(3)	N(4)···O(9A')	2.97(3)
N(4)···O(13A')	2.96(3)	N(6)···O(7A)	2.61(3)
N(10)···O(7B)	2.66(3)	N(11)···O(9B)	2.90(3)
N(11)···O(13B)	2.90(3)		
O(1)···O(2)	2.84(3)	O(2)···O(3)	2.87(3)
		N(4)···O(12A)	2.99(3)
		N(8)···O(5B)	2.66(3)
		N(11)···O(12B')	2.95(3)
		O(3)···O(1)	2.90(3)

the ideal value¹⁰ whereas the second one [O(1), O(4)] corresponds to larger values ranging from 2.49(2) to 2.54(2) [mean value 2.52(2)] Å. The latter values are close to those observed with protonated calixarene oxygen atoms;^{4,6,14} however, in the present case, the situation is quite different since the corresponding oxygen atoms are bridging two UO_2^{2+} ions [U(1) and U(3)] and must be deprotonated for charge equilibrium. These distances can be compared to that obtained for a bridging oxygen atom in the trinuclear complex of *p*-*tert*-butylcalix[6]arene, which is 2.54 Å.¹⁰ The co-ordination environment of U(1) is completed by a pseudo-trigonal μ_3 -oxo ion O^{2-} [O(14)] which bridges U(1), U(3) and U(3'), giving rise to a tetranuclear symmetry-centred core of a type which has been described with various extra ligands^{22–27} (some oxo-centred trinuclear species have also been reported^{10,28,29}). The U–O(14) distances range from 2.12(2) to 2.28(2) [mean value 2.21(6)] Å, in good agreement with the values reported in the literature (between 2.08 and 2.41 Å) as well as the $\text{U}\cdots\text{U}$ distances (mean value 3.80(6) Å, from 3.68 to 4.06 Å in the literature). However, whereas in the cases already reported the U_4O_2 core (or U_3O in the trinuclear species) is nearly planar, the UO_2^{2+} ions being roughly parallel to each other, some deviation from planarity is observed here (O(14) is ± 0.27 and ± 0.22 Å from the mean uranium plane in molecules A and B, respectively). This is likely a consequence of the U(1)O_2^{2+} ion being lengthened and strongly tilted with respect to U(3)O_2 , due to the presence of U(2), as will be seen hereafter. The whole tetranuclear assembly can be viewed as the condensation of four pentagonal bipyramids, sharing two [U(1)] or three [U(3)] edges. The dihedral angle between the basal planes of the bipyramids associated with U(1) and U(3) is 21.4 and 19.1° in A and B, respectively, this large value (the usual one is ≈ 5 –10°) being a consequence of the tilt of U(1)O_2 . The co-ordination polyhedron of U(3) is completed by one oxygen atom from each calixarene molecule [O(1), O(4')] with distances of 2.44(2) and 2.38(2) Å in A and B, respectively, slightly lower than the distances of the same atoms with U(1) and U(1'), and by the nitrogen atom of an acetonitrile molecule with U(3)–N(1) distances of 2.56(3) and 2.43(2) Å in A and B, respectively, to be compared to 2.53(3) Å previously observed in an acetonitrile adduct of uranyl ions.³⁰

The uranyl ion U(2)O_2^{2+} is in a somewhat less usual environment. It is surrounded in its equatorial plane by three oxygen atoms from the calixarene [O(5)–O(7)] with U–O distances ranging from 2.12(3) to 2.28(2) [mean value 2.24(6)] Å and, more surprisingly, by one of the oxygen atoms [O(8)] from the U(1)O_2^{2+} ion, which is involved in a long-short U(2)–O(8)=U(1) linkage and can be viewed as a dissymmetric μ -oxo bridge. Such an arrangement exists among inorganic compounds,³¹ and some rare examples have been reported among metal–organic complexes.^{32,33} The trinuclear uranyl complex of *p*-*tert*-butylcalix[8]arene obtained by Harrowfield and Ogden^{10,12} is a recent example in a system close to the present one. The U(2)–O(8) distances in A and B, 2.30(2) and 2.35(2) Å, respectively, are shorter than the values previously reported (2.42(3),³¹ 2.50(4),³² 2.49(7)³³ Å). The complexation of one of the oxygen atoms of the UO_2^{2+} moiety is not an unlikely event since it is known that the dipolar nature of the U=O bond results in an effective charge on the uranium atom larger than 2+, with the consequence of a partial δ^- charge on the oxygen atoms.³⁴ The hydrogen bond acceptor nature of the oxo atoms of uranyl^{4,6,7,14,34} results from the presence of this negative partial charge, which also confers a potential complexing ability upon these atoms. A slight effect of complexation on uranyl geometry can sometimes be detected. This is not the case in hydrogen triuranate, in which the U=O distance assumes its usual value (1.78(3) Å).³¹ However, in the trimeric compound bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)dioxouranium(VI), in which the three uranyl ions are bridged by three of their oxo atoms, the terminal U=O distances (about 1.70 Å)

are shorter than the bridging ones (about 1.80 Å).³² In the uranyl thiolate oxo cluster which constitutes the third reported example, these U=O (terminal) and U=O (bridging) distances are 1.771(7) and 1.838(7) Å, respectively, which indicates a slight but significant lengthening upon complexation.³³ A comparable lengthening has been reported in the case of a $\text{Na}^+\cdots\text{O}=\text{U}=\text{O}^{2+}\cdots\text{Na}^+$ complex, with U=O distances of 1.816(5) and 1.812(5) Å and $\text{O}\cdots\text{Na}$ distances of 2.392(6) and 2.357(6) Å.³⁵ A lengthening of the U=O bond upon complexation is also apparent in the present case, with distances U(1)–O(8) (mean value 1.88(3) Å) significantly larger than the other U(2)=O and U(3)=O distances, which lie in the usual range (mean value 1.77(3) Å). The U(1)–O(9) distances (mean value 1.815(7) Å) seem also slightly larger than the usual ones. The O(8)–U(1)–O(9) angles (mean value 179.1(1)°) do not indicate any deviation from linearity; this is in agreement with the results of solid state structure determinations³⁶ as well as relativistic extended Hückel calculations,³⁷ which show that the uranyl ion remains linear for U=O distances ranging from about 1.50 to more than 1.90 Å.

As a whole, the resulting hexanuclear cluster appears to have a nearly planar U(1)–U(3)–U(1')–U(3') core, with two oxo-bonded appendages [U(2), U(2')] located on each side, above and below the central plane. Such an arrangement is unprecedented and provides an example of one of the highest nuclearities obtained in calixarene complexes (an even larger assembly, the complex of an Eu_7 double-cubane cluster with *p*-*tert*-butylcalix[9]arene, has however been obtained¹⁰). It represents also one of the highest nuclearities in dioxouranium(VI) assemblies, apart from the frequent polymeric chain arrangement of uranyl ions; another uranyl hexanuclear complex has been reported, which is also based on the oxo-centred trinuclear motif but in which two such moieties are linked by two azido bridges.²⁹

The complex core $(\text{UO}_2^{2+})_6(\text{L}^{7-})_2(\text{O}^{2-})_2$ bears a 6– charge, which is equilibrated by six protonated DABCO molecules. Four are located on the external sides of the molecule and are hydrogen bonded to the phenolic oxygen atoms O(5), O(7), O(5') and O(7'), which are also bonded to U(2) and U(2'). The other two are located between the two calixarene molecules, on each side of the cluster mean plane and potentially hydrogen bonded to three uranyl oxygen atoms each; the three $\text{N}\cdots\text{O}$ (uranyl) distances (mean value 2.97(2) Å) are rather large with respect to the distances found with triethylamine (mean value 2.76(6) Å)^{4,6,7,14} since none of them corresponds to a linear hydrogen bond. Many solvent molecules (CH_3CN , CHCl_3 , CH_3OH , H_2O) are located in the intermolecular voids, which may explain the low stability of the crystals; the three water molecules [O(1)–O(3)] make an isolated triangular hydrogen-bonded assembly.

The calixarene conformation deserves some comments. Up to now, three structures of R-calix[7]arenes only are known, two of uncomplexed species, with $\text{R} = p$ -ethyl³⁸ and *p*-*tert*-butyl (pyridine adduct)³⁹ and that of the uranyl complex previously cited.⁷ In all of them the overall calixarene conformation is the same and can be described as the juxtaposition of a tetrameric and a trimeric subunit, which both assume a cone shape. This is particularly evident from the sequence of φ and χ torsion angles, as defined by Uguzzoli and Andreotti,⁴⁰ which is of the $+-+-$ type in each subunit and $-+$ at the junction between them. In the present case the conformation is quite different, as indicated by the torsion angles reported in Table 3. As shown in Fig. 3, two subunits, tetrameric [O(1)–O(4)] and trimeric [O(5)–O(7)], are still clearly defined; the trimeric one, which encapsulates U(2), is in the cone conformation as usual, but the tetrameric one, bonded to U(1), corresponds to a $+- -+ +-$ sequence, analogous to that found in the dinuclear uranyl complex of *p*-*tert*-butylcalix[8]arene.⁴ The junction between the two subunits corresponds to a sign reversal of the torsion angles (one of them being very far from its ideal '*gauche*' value) and

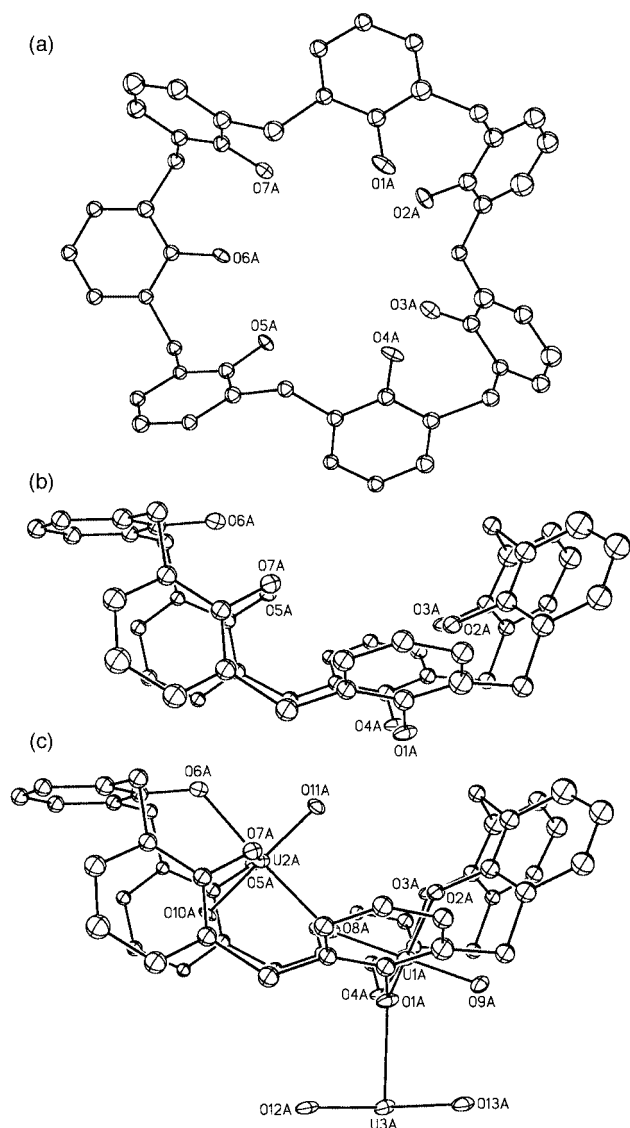


Fig. 3 Three views of the calixarene moiety, without (a, b) or with (c) uranyl ions (molecule A). Hydrogen atoms and *p*-benzyl substituents omitted for clarity.

also by a large O...O separation (Table 2). The whole calixarene conformation is derived from the usual one by the upside-down reversing of the units 1 and 4. The dihedral angle between the planes defined by O(1)–O(4) and O(5)–O(7) is 63° in both A and B, to be compared to 90.5–90.8° in the usual conformation.^{7,39} The present complex can be viewed as half a dinuclear *p*-*tert*-butylcalix[8]arene complex associated with a trimeric cone complex. The two uranyl ions are so close and so tilted with respect to each other that a direct linkage between them ensues. In the mononuclear uranyl complex of *p*-*tert*-butylcalix[7]arene previously reported⁷ the tetrameric subunit only is active in complexation, which leaves an unoccupied space in the molecule. Both subunits are complexed in **1**, owing to a conformation change. The present result shows that the calix[7]arene core is not large enough to accommodate two nearly parallel ions like the calix[8]arene one. It likely represents the border between mono- and di-nuclear complexation, whereas calix[6]arene is definitely too small to encapsulate two uranyl ions.

The question arises of the reasons why such striking differences exist between complex **1** and the mononuclear uranyl complex of *p*-*tert*-butylcalix[7]arene (in which case the 2:1 metal:ligand stoichiometry used during the synthesis was not kept in the solid state). One may suspect two obvious sources from which they could originate, which are the replacement of *tert*-butyl by benzyl *p*-substituents and the replacement of NEt₃

Table 3 Selected torsion angles (°)

Rings	A		B	
	ϕ	χ	ϕ	χ
1–2	–75	118	73	–118
2–3	90	–91	–85	83
3–4	–122	74	119	–75
4–5	–21	112	19	–109
5–6	76	–84	–79	94
6–7	83	–80	–91	77
7–1	–106	26	112	–21

by DABCO as a deprotonating agent. The former increases the acidity of the phenolic protons, since benzyl is a less effective electron-donor substituent than *tert*-butyl, which is consistent with the degrees of deprotonation observed (four in the mononuclear complex and seven in **1**), whereas the pK_a values of the bases used, 11.01 for NEt₃ and 2.95 and 8.60 for DABCO, should imply a lower deprotonation degree in the second case. Obviously, the nature of the base is not the principal factor that makes the degree of calixarene deprotonation different in the two cases and the increase in calixarene acidity seems to be predominant (it has been noted that uranyl ion complexation may enhance the phenolic groups acidity;^{2,6} however, this effect must be of comparable importance in the two present cases). It is likely that a higher deprotonation degree, which affects the trimeric subunit in *p*-benzylcalix[7]arene, makes more easy the complexation of multiple species. As a second-order effect, the replacement of *tert*-butyl by benzyl groups may also increase the hydrophobicity of the reacting medium, which could increase the stability of uranyl clusters in solution. As a confirmation of the predominant effect of substituent replacement, it may be noted that, when DABCO is used during the synthesis of the *p*-*tert*-butylcalix[8]arene complex, it results in a dinuclear species whose structure is the same as that obtained in the presence of NEt₃,† the two compounds only differing by the solvent molecules and counter ions that surround the complex core, with 6.5 DABCO molecules making an extended hydrogen bonding network with calixarenes, nitrate ions and other solvent molecules in the second case. It is dubious, however, that a higher deprotonation degree in *p*-*tert*-butylcalix[8]arene could lead to completely different species, the ditopic potential of this ligand being fulfilled in all the cases. Harrowfield¹⁰ previously reported that, when replacing NEt₃ by NMe₄OH during the synthesis of the uranyl complex of *p*-*tert*-butylcalix[8]arene, a trinuclear complex was obtained instead of the dinuclear one, but, since the third uranyl ion has no contact with the calixarene moiety, this effect is not directly comparable to the one described here. Unfortunately, it has been impossible up to now to grow single crystals of the cross-species (*p*-*tert*-butylcalix[7]arene with DABCO and *p*-benzylcalix[7]arene with NEt₃) which would help to make this point clearer. Obviously, even if the ring-size effects begin to be correctly understood, much work remains to be done to get the complexing properties of these systems under satisfactory control.

† Crystal data: C₂₆₁H₄₂₁Cl₃N₃₀O₅₂U₄, $M = 5869.75$, monoclinic, space group $P2_1/c$, $a = 22.491(3)$, $b = 37.201(4)$, $c = 34.568(3)$ Å, $\beta = 90.960(4)^\circ$, $V = 28919(4)$ Å³, $T = 123$ K, $Z = 4$.⁴¹

References

- S. Shinkai, H. Koreishi, K. Ueda, T. Arimura and O. Manabe, *J. Am. Chem. Soc.*, 1987, **109**, 6371.
- J. M. Harrowfield, M. I. Ogden and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1991, 979.
- J. M. Harrowfield, M. I. Ogden and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1991, 2625.
- P. Thuéry, N. Keller, M. Lance, J. D. Vigner and M. Nierlich, *Acta Crystallogr., Sect. C*, 1995, **51**, 1570; *New J. Chem.*, 1995, **19**, 619.

- 5 P. Thuéry, M. Lance and M. Nierlich, *Supramol. Chem.*, 1996, **7**, 183.
- 6 P. Thuéry and M. Nierlich, *J. Inclusion. Phenom.*, 1997, **27**, 13.
- 7 P. Thuéry, M. Nierlich, M. I. Ogden and J. M. Harrowfield, *Supramol. Chem.*, 1998, **9**, 297.
- 8 P. D. Beer, M. G. B. Drew, D. Heseck, M. Kan, G. Nicholson, P. Schmitt, P. D. Sheen and G. Williams, *J. Chem. Soc., Dalton Trans.*, 1998, 2783.
- 9 P. C. Leverd, P. Berthault, M. Lance and M. Nierlich, *Eur. J. Inorg. Chem.*, 1998, 1859.
- 10 J. Harrowfield, *Gazz. Chim. Ital.*, 1997, **127**, 663.
- 11 X. Delaigue, J. M. Harrowfield, M. I. Ogden and A. H. White, manuscript in preparation.
- 12 M. I. Ogden and J. M. Harrowfield, unpublished result.
- 13 C. D. Gutsche, D. F. Stewart, J. M. Harrowfield and M. I. Ogden, to be published.
- 14 P. Thuéry and M. Nierlich, *J. Chem. Soc., Dalton Trans.*, 1997, 1481.
- 15 B. Souley, Z. Asfari and J. Vicens, *Pol. J. Chem.*, 1992, **66**, 959.
- 16 Kappa-CCD Software, Nonius B. V., Delft, 1998.
- 17 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.
- 18 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 19 G. M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures, University of Göttingen, 1993.
- 20 A. L. Spek, PLATON, University of Utrecht, 1998.
- 21 G. M. Sheldrick, SHELXTL, University of Göttingen, (distributed by Bruker AXS, Madison, WI) 1997.
- 22 M. Åberg, *Acta Chem. Scand., Sect. A*, 1976, **30**, 507.
- 23 A. Perrin and J. Y. Le Marouille, *Acta Crystallogr., Sect. B*, 1977, **33**, 2477.
- 24 A. Perrin, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1169.
- 25 A. J. Zozulin, D. C. Moody and R. R. Ryan, *Inorg. Chem.*, 1982, **21**, 3083.
- 26 G. Van den Bossche, M. R. Spirlet, J. Rebizant and J. Goffart, *Acta Crystallogr., Sect. C*, 1987, **43**, 837.
- 27 U. Turpeinen, R. Hämäläinen, I. Mutikainen and O. Orama, *Acta Crystallogr., Sect. C*, 1996, **52**, 1169.
- 28 R. L. Lintvedt, M. J. Heeg, N. Ahmad and M. D. Glick, *Inorg. Chem.*, 1982, **21**, 2350.
- 29 P. Charpin, M. Lance, M. Nierlich, D. Vigner, J. Livet and C. Musikas, *Acta Crystallogr., Sect. C*, 1986, **42**, 1691.
- 30 T. J. Hall, C. J. Mertz, S. M. Bachrach, W. G. Hipple and R. D. Rogers, *J. Cryst. Spectrosc. Res.*, 1989, **19**, 499.
- 31 S. Siegel, A. Viste, H. R. Hoekstra and B. Tani, *Acta Crystallogr., Sect. B*, 1972, **28**, 117.
- 32 J. C. Taylor, A. Ekstrom and C. H. Randall, *Inorg. Chem.*, 1978, **17**, 3285.
- 33 D. Rose, Y. D. Chang, Q. Chen and J. Zubietta, *Inorg. Chem.*, 1994, **33**, 5167.
- 34 T. S. Franczyk, K. R. Czerwinski and K. N. Raymond, *J. Am. Chem. Soc.*, 1992, **114**, 8138.
- 35 D. M. Barnhart, C. J. Burns, N. N. Sauer and J. G. Watkin, *Inorg. Chem.*, 1995, **34**, 4079.
- 36 R. G. Denning, in *Gmelin Handbook of Inorganic Chemistry, Uranium*, Supplement Vol. A6, 8th edn, Springer, Berlin, 1983, p. 31.
- 37 P. Pyykkö, L. J. Laakkonen and K. Tatsumi, *Inorg. Chem.*, 1989, **28**, 1801.
- 38 M. Perrin, S. Lecocq and Z. Asfari, *C. R. Acad. Sci. Paris*, 1990, **310**, 515.
- 39 G. D. Andreotti, F. Ugozzoli, Y. Nakamoto and S. I. Ishida, *J. Inclusion Phenom.*, 1991, **10**, 241.
- 40 F. Ugozzoli and G. D. Andreotti, *J. Inclusion Phenom.*, 1992, **13**, 337.
- 41 P. Thuéry and M. Nierlich, unpublished results.

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