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Uranyl ion complexation by medium and large homooxacalixarenes: from mono- to poly-uranate complexes

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Received 22nd November 2000, Accepted 26th January 2001
First published as an Advance Article on the web 22nd February 2001

Crystal structures of dioxouranium(VI) complexes of three homooxacalix[*n*]arenes ($n = 4$, 6 or 8) have shown the possibility to complex metal moieties of variable nuclearity, depending upon the number of phenolic groups and ether links they contain. *p-tert*-Butyltetrahomodioxacalix[6]arene embraces a single uranyl unit through tetraphenoxide coordination as commonly observed in calixarene complexes, whereas *p*-methyloctahomotetraoxacalix[4]arene binds a doubly bridged binuclear species coordinated to both phenoxide and ether oxygen donors, while the large *p-tert*-butyloctahomotetraoxacalix[8]arene binds a unique tetrauranate cluster containing both double and single oxygen bridges between uranium atoms and involving only phenoxide-oxygen coordination to the macrocycle. An additional crystal structure determination on the triethylammonium complex of the singly deprotonated homooxacalix[6]arene enables some comments to be made on the effects of coordination on the macrocycle conformation. The relation between the nuclearity of the uranyl complexes with ligands in the calixarene/homooxacalixarene family and the size of the ligands is discussed.

The complexing properties of homooxacalixarenes, in which one or more CH_2OCH_2 ether links replace the methylene bridges of ordinary calixarenes,[1] have relatively little been explored. In part, this reflects the limited range of homooxacalixarenes first known, but early studies of homooxacalixarene synthesis[2] have recently been considerably extended,[3–5] providing such macrocycles, in good yields, with sizes up to that of calix[12]arene, and inviting further investigation of their coordination chemistry. Furthermore, the range of molecules with a given number of phenolic units is larger than with classical calixarenes due to the variation in number and position of the ether links. Significantly, though calix[*n*]arenes up to $n = 20$ have been characterized,[6] little is known of the coordination chemistry for species with $n > 12$. Relatively long-known structural work on homooxacalixarene complexes[3] concerns only dihomooxacalix[4]arene and hexahomotrioxacalix[3]arene derivatives as ligands, with only two studies of uranyl ion complexes,[7,8] among alkali-metal, transition-metal and lanthanide ion complexes. One of those uranyl complex structures demonstrated a unique pseudo-trigonal coordination of this ion[8] not seen in any of the relatively numerous complexes with calix[*n*]arenes ($n = 5$–8) studied earlier.[9] A recent study of *p-tert*-butyltetrahomodioxacalix[4]arene,[10,11] however, has shown that its uranyl ion complex displays the same tetradentate, phenoxide-*O* binding of the ligand seen in several simple calixarene complexes, so the present work was undertaken further to explore the U^{VI}-complexing properties of homooxacalixarenes, especially the larger members of the series, in terms of number of either phenolic groups or ether links. The ligands involved are *p-tert*-butyltetrahomodioxacalix[6]arene **1**, *p*-methyloctahomotetraoxacalix[4]arene **2** and *p-tert*-butyloctahomotetraoxacalix[8]arene **3**. Using a notation based upon the number of atoms in the bridges between phenolic rings in the macrocycle,[12] these can be designated [3.1.3.1.1.1]-, [3.3.3.3]- and [3.1.3.1.3.1.3.1]-homooxacalixarenes, respectively. To the best of our knowledge, this is the first crystal structure determination for any of these three molecules.

Experimental

Synthesis

***p-tert*-Butyltetrahomodioxacalix[6]arene 1.** This compound was synthesized as reported elsewhere.[4] Calc. for $C_{38}H_{53}NO_4$: C, 77.64; H, 9.09. Found: C, 77.53; H, 9.12%. ^1H NMR (300 MHz, $CDCl_3$, referenced to TMS): δ 1.24 (s, 18H, *t*-Bu), 1.25 (s, 18H, *t*-Bu), 1.26 (s, 18H, *t*-Bu), 3.80–4.15 (br, 8H, $ArCH_2Ar$), 4.66 (br s, 8H, $ArCH_2OCH_2Ar$), 6.97 (d, $J = 2.4$, 2H, Ar), 7.00 (d, $J = 2.4$, 2H, Ar), 7.17 (s, 4H, Ar), 7.25 (d, $J = 2.4$, 2H, Ar), 7.34 (d, $J = 2.4$ Hz, 2H, Ar), 8.43 (s, 2H, OH), 9.34 (s, 2H, OH) and 10.14 (s, 2H, OH). Slow evaporation of a solution of **1** (0.030 g, 0.029 mmol) in 5 ml of $CHCl_3$–CH_3CN (1 : 1) with a large excess (5 ml) of NEt_3 afforded colourless single crystals of $[(\mathbf{1} - H)(HNEt_3)]\cdot CH_3CN$ **4** of low quality but suitable for structure determination by X-ray crystallography.

***p*-Methyloctahomotetraoxacalix[4]arene 2.** This was synthesized as reported elsewhere.[5] Calc. for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.94; H, 7.06%. ^1H NMR (200 MHz, $CDCl_3$ referenced to TMS): δ 2.20 (s, 12H, Me), 4.67 (s, 16H, $ArCH_2OCH_2Ar$), 6.92 (s, 8H, Ar) and 8.11 (4H, ArO*H*).

***p-tert*-Butyloctahomotetraoxacalix[8]arene 3.** This was synthesized as previously reported.[4] Calc. for $C_{23}H_{30}O_3$: C, 77.93; H, 8.53. Found: C, 77.64; H, 8.76%. ^1H NMR (200 MHz, $CDCl_3$, referenced to TMS): δ 1.22 (s, 72H, *t*-Bu), 4.04 (s, 8H, $ArCH_2Ar$), 4.63 (s, 16H, $ArCH_2OCH_2Ar$), 6.93 (d, $J = 2.0$, 8H, Ar), 7.22 (d, $J = 2.0$ Hz, 8H, Ar) and 9.06 (s, 8H, OH).

DOI: 10.1039/b009364p

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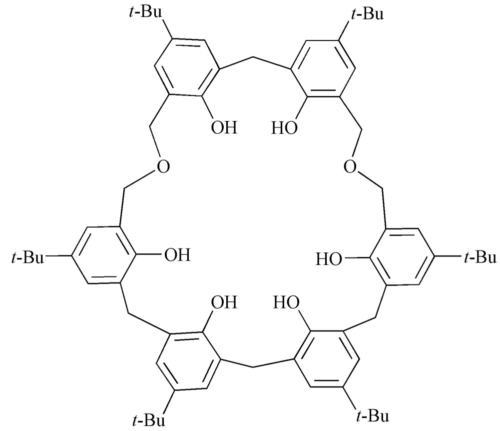

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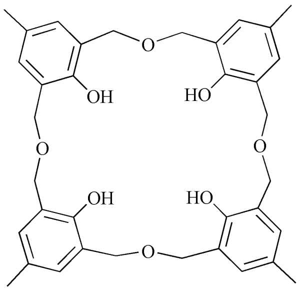

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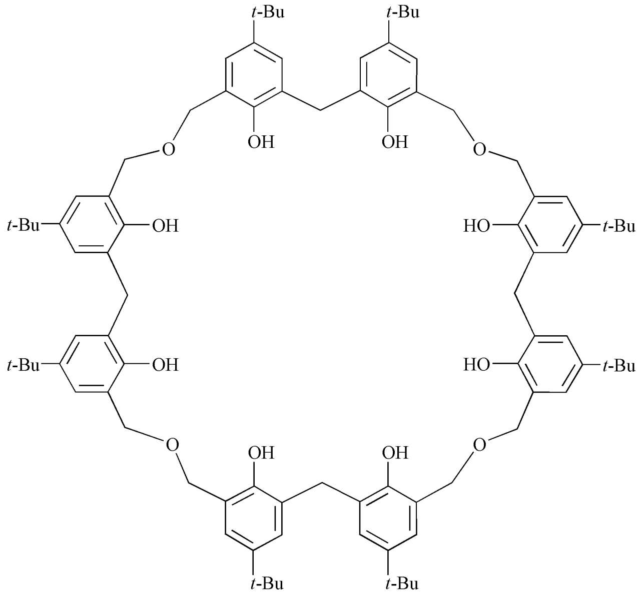

3

[HNEt$_3$]$_2$[UO$_2$(1 − 4H)]·3CH$_3$CN 5. Compound **1** (0.040 g, 0.039 mmol) was dissolved in 10 ml of CH$_3$CN and 4 ml of NEt$_3$. A solution of UO$_2$(NO$_3$)$_2$·6H$_2$O (0.040 g, 0.08 mmol) in 5 ml of CH$_3$CN was then added dropwise, giving immediately an orange solution, which, on slow evaporation, afforded a few orange single crystals suitable for X-ray crystallography. Microanalysis results on samples including both crystals and powder were unsatisfactory due to the heterogeneous nature of the latter. FAB-MS: *m*/*z* 1300 corresponding to [UO$_2$(C$_{68}$H$_{84}$O$_8$) + 2H$^+$].

[C$_5$H$_5$NH][(UO$_2$)$_2$(2 − 4H)(OH)(H$_2$O)]·2.5C$_5$H$_5$N 6. Compound **2** (0.023 g, 0.038 mmol) was dissolved in 20 ml of pyridine. A solution of UO$_2$(NO$_3$)$_2$·6H$_2$O (0.080 g, 0.16 mmol) in 20 ml of pyridine was then added dropwise, giving immediately an orange solution, which, on slow evaporation, afforded beautiful orange single crystals suitable for X-ray diffraction. Calc. for C$_{107}$H$_{115}$N$_7$O$_{28}$U$_4$: C, 44.33; H, 4.00. Found: C, 43.82; H, 3.97%.

[HNEt$_3$]$_2$[(UO$_2$)$_4$(3 − 8H)(OH)$_2$(H$_2$O)$_4$]·1.5NEt$_3$·2.5H$_2$O·CH$_3$OH 7. Compound **3** (0.030 g, 0.021 mmol) was dissolved in 5 ml of CH$_3$CN and 2 ml of NEt$_3$. A solution of UO$_2$(NO$_3$)$_2$·6H$_2$O (0.060 g, 0.12 mmol) in 5 ml of CH$_3$CN was then added dropwise, giving immediately an orange solution. The solid formed was recrystallized several times from mixtures of CH$_3$CN, CHCl$_3$ and CH$_3$OH and finally afforded, on slow evaporation, a few orange single crystals of low quality which only permitted the determination of a rough crystal structure by X-ray diffraction. This structure is reported herein, in spite of its low accuracy, due to its chemical interest. All attempts to grow better crystals from other preparations have been unsuccessful. Microanalysis results on samples including both crystals and powder were unsatisfactory due to the heterogeneous nature of the latter. ^{1}H NMR (200 MHz, CDCl$_3$, referenced to TMS): δ 1.41 (s, 36H, *t*-Bu), 1.42 (s, 36H, *t*-Bu), 3.55 (d, $J = 13.3$, 4H, ArC*H*$_2$Ar), 5.08 (d, $J = 13.8$, 8H, ArC*H*$_2$OC*H*$_2$Ar), 5.46 (d, $J = 13.3$, 4H, ArC*H*$_2$Ar), 6.21 (d, $J = 13.8$, 8H, ArC*H*$_2$OC*H*$_2$Ar), 7.43 (d, $J = 2.0$, 8H, Ar), 7.72 (d, $J = 2.0$ Hz, 8H, Ar) and 9.06 (s, 8H, OH). FAB-MS: *m*/*z* 2489.7 corresponding to [(UO$_2$)$_4$(**3** − 8H) + 2H$^+$].

Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer[13] using graphite-monochromated Mo-Kα radiation (λ 0.71073 Å). The crystals were introduced in Lindemann glass capillaries with a protecting "Paratone" oil (Exxon Chemical Ltd.) coating. The data were processed with DENZO-SMN.[14] The structures were solved by direct methods with SHELXS 97[15] and subsequent Fourier-difference synthesis and refined by full-matrix least squares on F^2 with SHELXL 97.[16] No absorption correction was done for compound **4**. Absorption effects in **5**, **6** and **7** were corrected empirically with the program MULABS from PLATON.[17] Hydroxyl and ammonium protons in **4** were introduced as found on the Fourier-difference maps whereas they were not found, nor introduced, in the other compounds. All other hydrogen atoms in compounds **4**–**6** were introduced at calculated positions, except in the disordered parts when present and in some solvent molecules. Hydrogen atoms were not introduced in **7**. All hydrogen atoms were treated as riding atoms with a displacement parameter equal to 1.2 (OH, NH, CH, CH$_2$) or 1.5 (CH$_3$) times that of the parent atom. All non-hydrogen atoms were refined anisotropically in **4**–**6**, except the disordered ones in **4** and **5** and the carbon atoms of the aromatic rings in **5** in order to keep the number of parameters within the limits of the full-matrix least-squares refinement. In **7** uranium, oxygen and nitrogen atoms only have been refined anisotropically for the same reason. Special features for each compound are indicated in the following.

4. Three *tert*-butyl groups were found disordered and were modelled with five or six terminal carbon atoms. The acetonitrile solvent molecule is disordered over two positions, its terminal carbon atom being located on a symmetry centre.

5. Two *tert*-butyl substituents and the methylenic carbon atoms of one triethylammonium cation were found disordered over two positions each, which have been refined with occupation factors constrained to sum to unity.

6. One pyridine molecule is disordered around a symmetry centre (and hence the nitrogen atom is not located). The protons of OH$^-$, H$_2$O and that of the pyridinium ion have not been found on the Fourier-difference map, nor introduced.

Table 1 Crystal data and structure refinement details for compounds **4**–**7**

	4	**5**	**6**	**7**
Empirical formula	$C_{76}H_{106}N_2O_8$	$C_{86}H_{125}N_5O_{10}U$	$C_{53.5}H_{57.5}N_{3.5}O_{14}U_2$	$C_{114}H_{185.5}N_{3.5}O_{29.5}U_4$
M/g mol^{-1}	1175.63	1626.94	1449.59	3029.28
T/K	110(2)	110(2)	100(2)	110(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	20.835(2)	17.5673(5)	11.2810(4)	42.749(9)
b/Å	10.1184(6)	29.527(2)	25.648(2)	17.169(5)
c/Å	32.366(3)	33.032(2)	17.961(1)	43.577(10)
β/°	91.815(3)	99.590(3)	98.454(3)	117.83(1)
V/Å^3	6820(1)	16895(2)	5140(1)	28285(5)
Z	4	8	4	8
μ/mm^{-1}	0.073	1.979	6.364	4.629
Reflections collected	44684	101135	33418	81335
Independent reflections	12162	29617	8887	23002
Observed reflections [$I > 2\sigma(I)$]	4359	16819	5945	3777
R_{int}	0.148	0.138	0.103	0.084
$R1$	0.103	0.067	0.051	0.116
$wR2$	0.217	0.128	0.110	0.149

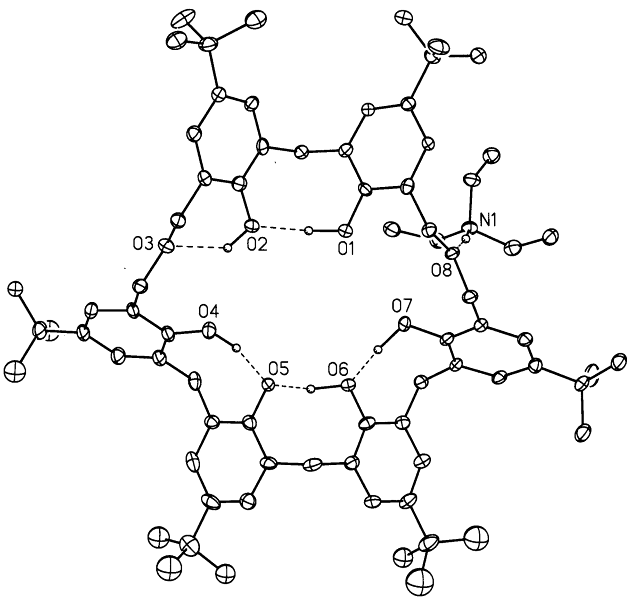

Fig. 1 View of *p-tert*-butyltetrahomodioxacalix[6]arene **1** in **4**. Hydrogen bonds as dashed lines. Hydroxyl and ammonium protons represented as small spheres of arbitrary radii. Other hydrogen atoms and solvent molecule omitted for clarity. Only the main component of disordered parts is represented.

7. The aromatic rings have been refined as idealized hexagons. One of the triethylammonium cations, being unstable, has been fixed in the last refinement cycles.

Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with SHELXTL.[18] All calculations were performed on Silicon Graphics R5000 and R12000 workstations.

CCDC reference numbers 153523–153526.

See http://www.rsc.org/suppdata/dt/b0/b009364p/ for crystallographic data in CIF or other electronic format.

Results and discussion

It is useful to consider first the structure of the singly deprotonated form of ligand **1**, in the form of the hydrogen bound triethylammonium ion complex [(**1** − H)($HNEt_3$)]·CH_3CN **4**, represented in Fig. 1, as a background to analysing conformational changes seen in the formation of the uranyl ion complex. The 3-atom ether linkages of the macrocycle are such that it may be considered composed of di- and tetra-phenolic units of an ordinary calixarene, with the monoanion in the solid seemingly possessing a non-crystallographic symmetry plane, perpendicular to the mean molecular plane and containing the methylene carbon atoms at the centres of these two units. This pseudo-symmetry plane is no longer valid when one considers the hydrogen bonding pattern. Hydrogen bonding of the tetraphenolic unit appears to be entirely internal, whereas the diphenolic unit has one bridging hydrogen bond and another linking it to an ether oxygen (Table 2). The other ether oxygen atom is involved in an hydrogen bond to the triethylammonium cation, which lies outside the macrocyclic cavity (though possibly interacting with two phenolic rings). The tetraphenolic unit has a conformation equivalent to that of half a calix[8]arene in its usual *pleated loop* conformation, with deprotonation formally at O(5). The O···O distances between the terminal oxygen atoms of each subunit are long, O(2)···O(4), 3.413(6) and O(1)···O(7) 3.492(6) Å, precluding any strong interaction (a weak one is however possible in the case of O(2)–H···O(4), since the estimated H···O(4) distance, 2.56 Å, is slightly lower than the sum of ionic radii (2.6 Å), but is impossible for O(1)···O(7) due to the position of the hydrogen atoms). This is in contrast with bifurcated hydrogen bonds involving a phenolic proton linked to both phenolic and ether oxygen atoms found in *p-tert*-butyltetrahomodioxacalix[4]arene, presumably as a result of its different ether-bridge conformation.[10,11]

The rather regular and symmetrical geometry observed in complex **4** is broken upon uranyl complexation in the presence of triethylamine. The binding of uranyl ion to ligand **1** enhances its acidity to the point where triethylamine removes four protons, generating the complex $[HNEt_3]_2[UO_2$(**1** − 4H)]·$3CH_3CN$ **5**, where the ligand adopts a completely asymmetric conformation, as illustrated in Fig. 2 with one of the two crystallographically independent (but nearly identical) molecules in the asymmetric unit. The uranyl cation is bound to two phenoxide groups from each subunit of the macrocycle, with U–O(phenoxide) bond lengths as usual[7–10] (Table 2, mean value 2.26(4) Å, including both molecules). The equatorial environment of the cation is a distorted square plane, the O(1)–U–O(7) angle being larger than the other ones due to the presence of the ether bridge O(8). The uranium ions are essentially coplanar with the four phenoxide donors, being located at 0.002(3) and 0.015 (3) Å from the mean planes defined by the four donor atoms in molecules A and B, respectively (rms deviation of fitted atoms 0.147 and 0.153 Å). The overall coordination environment is closely similar to that observed for several complexes of ordinary calixarenes.[9h] It also resembles that found in previous homooxacalixarene complexes[7,8,10] in that there is no apparent interaction with the ether-oxygen donors [U···O(8) 3.881(7) and 3.784(8) Å in molecules A and B, respectively (2.945–3.832 Å in earlier-known species)]. There

Table 2 Selected bond lengths (Å) and angles (°) in compounds **4**–**7**

Uranium environment							
5							
U(1)–O(1A)	2.203(5)	O(1A)–U(1)–O(2A)	83.5(2)	U(2)–O(1B)	2.213(6)	O(1B)–U(2)–O(2B)	85.9(2)
U(1)–O(2A)	2.244(5)	O(2A)–U(1)–O(6A)	90.4(2)	U(2)–O(2B)	2.246(5)	O(2B)–U(2)–O(6B)	88.7(2)
U(1)–O(6A)	2.301(6)	O(6A)–U(1)–O(7A)	86.0(2)	U(2)–O(6B)	2.301(6)	O(6B)–U(2)–O(7B)	85.3(2)
U(1)–O(7A)	2.285(5)	O(7A)–U(1)–O(1A)	101.2(2)	U(2)–O(7B)	2.288(5)	O(7B)–U(2)–O(1B)	101.2(2)
U(1)–O(9A)	1.786(5)	O(9A)–U(1)–O(10A)	176.8(2)	U(2)–O(9B)	1.780(5)	O(9B)–U(2)–O(10B)	177.9(3)
U(1)–O(10A)	1.815(6)			U(2)–O(10B)	1.811(5)		
6							
U(1)–O(1)	2.245(7)	O(1)–U(1)–O(2)	70.9(2)	U(2)–O(5)	2.260(7)	O(5)–U(2)–O(6)	70.3(2)
U(1)–O(2)	2.661(6)	O(2)–U(1)–O(3)	70.2(2)	U(2)–O(6)	2.685(6)	O(6)–U(2)–O(7)	70.7(2)
U(1)–O(3)	2.256(7)	O(3)–U(1)–O(14)	73.6(2)	U(2)–O(7)	2.221(7)	O(7)–U(2)–O(13)	82.3(3)
U(1)–O(9)	1.795(6)	O(14)–U(1)–O(13)	67.2(3)	U(2)–O(11)	1.801(6)	O(13)–U(2)–O(14)	67.0(3)
U(1)–O(10)	1.774(6)	O(13)–U(1)–O(1)	82.6(3)	U(2)–O(12)	1.789(6)	O(14)–U(2)–O(5)	74.4(2)
U(1)–O(13)	2.334(7)	O(9)–U(1)–O(10)	177.1(3)	U(2)–O(13)	2.340(7)	O(11)–U(2)–O(12)	177.2(3)
U(1)–O(14)	2.492(7)	U(1)–O(13)–U(2)	114.7(3)	U(2)–O(14)	2.502(7)	U(1) –O(14) –U(2)	104.0(3)
U(1)···U(2)	3.9359(4)						
7							
U(1A)–O(1A)	2.34(2)	U(2A)–O(4A)	2.38(5)	U(3A)–O(7A)	2.20(5)	U(4A)–O(10A)	2.35(5)
U(1A)–O(2A)	2.31(5)	U(2A)–O(5A)	2.16(2)	U(3A)–O(8A)	2.32(4)	U(4A)–O(11A)	2.25(5)
U(1A)–O(13A)	1.81(5)	U(2A)–O(15A)	1.72(6)	U(3A)–O(17A)	1.750(12)	U(4A)–O(19A)	1.79(5)
U(1A)–O(14A)	1.68(1)	U(2A)–O(16A)	1.86(1)	U(3A)–O(18A)	1.753(12)	U(4A)–O(20A)	1.68(5)
U(1A)–O(21A)	2.49(6)	U(2A)–O(21A)	2.40(6)	U(3A)–O(22A)	2.51(6)	U(4A)–O(22A)	2.58(6)
U(1A)–O(23A)	2.34(5)	U(2A)–O(25A)	2.47(5)	U(3A)–O(25A)	2.44(2)	U(4A)–O(23A)	2.40(2)
U(1A)–O(24A)	2.55(2)	U(2A)–O(26A)	2.33(5)	U(3A)–O(26A)	2.22(5)	U(4A)–O(24A)	2.55(2)
U(1B)–O(1B)	2.22(4)	U(2B)–O(4B)	2.21(4)	U(3B)–O(7B)	2.23(4)	U(4B)–O(10B)	2.29(4)
U(1B)–O(2B)	2.23(5)	U(2B)–O(5B)	2.16(5)	U(3B)–O(8B)	2.28(4)	U(4B)–O(11B)	2.11(5)
U(1B)–O(13B)	1.81(5)	U(2B)–O(15B)	1.78(4)	U(3B)–O(17B)	1.79(5)	U(4B)–O(19B)	1.78(4)
U(1B)–O(14B)	1.72(5)	U(2B)–O(16B)	1.70(5)	U(3B)–O(18B)	1.84(4)	U(4B)–O(20B)	1.68(1)
U(1B)–O(21B)	2.70(5)	U(2B)–O(21B)	2.39(5)	U(3B)–O(22B)	2.50(4)	U(4B)–O(22B)	2.43(4)
U(1B)–O(23B)	2.40(4)	U(2B)–O(25B)	2.48(4)	U(3B)–O(25B)	2.54(4)	U(4B)–O(23B)	2.43(2)
U(1B)–O(24B)	2.52(4)	U(2B)–O(26B)	2.43(4)	U(3B)–O(26B)	2.35(4)	U(4B)–O(24B)	2.47(4)
Mean values for the eight uranyl ions in **7**[a]							
U–O(phenol)	2.25(8)	O(uranyl)–U–O (uranyl)	177(3)	U···U(sb)	4.96(10)	U···U···U	90(1)
U–O(uranyl)	1.76(6)	U–O(sb)–U	164(2)	U···U(db)	4.08(3)		
U–O(sb)	2.50(9)	U–O(dbi)–U	109(1)				
U–O(dbi)	2.50(4)	U–O(dbe)–U	120(4)				
U–O(dbe)	2.36(7)						
Hydrogen bonds							
4							
O(1)···O(2)	2.776(6)	O(1)–H	1.10	H···O(2)	1.69	O(1)–H···O(2)	168
O(2)···O(3)	2.691(6)	O(2)–H	0.98	H···O(3)	1.96	O(2)–H···O(3)	130
O(4)···O(5)	2.545(5)	O(4)–H	1.09	H···O(5)	1.51	O(4)–H···O(5)	158
O(6)···O(5)	2.466(5)	O(6)–H	1.18	H···O(5)	1.30	O(6)–H···O(5)	166
O(7)···O(6)	2.605(6)	O(7)–H	1.15	H···O(6)	1.46	O(7)–H···O(6)	174
N(1)···O(8)	2.794(6)	N(1)–H	1.09	H···O(8)	1.71	N(1)–H···O(8)	172
5							
O(4A)···O(5A)	2.653(8)	O(5A)···O(6A)	2.540(8)	O(4B)···O(5B)	2.662(8)	O(5B)···O(6B)	2.570(8)
N(1)···O(10A)	2.727(10)	N(3)···O(7A)	2.768(9)	N(2)···O(10B)	2.672(9)	N(4)···O(7B)	2.811(8)
6							
N(1)···O(8)	2.802(11)	N(1)···O(12)	2.944(11)	N(2)···O(13)	2.709(11)	N(3)···O(14)	2.635(11)
7[b]							
N(1)···O(14A)	2.81(3)	N(2)···O(17A)	3.00(2)	N(3)···O(5B)	2.80(4)	N(4)···O(14B)	2.89(4)

[a] The values in parentheses indicate the dispersion; sb = single bridge, dbi = double bridge (internal), dbe = double bridge (external). [b] The hydrogen bonds involving calixarene oxygen atoms and triethylammonium ions are reported only.

is a particularly close resemblance between the part of the ligand including atoms O(1), O(7) and O(6) and the analogous section of the uranyl ion complex of *p*-*tert*-butyldihomooxacalix[4]arene ([3.1.1.1]homooxacalixarene),[7] with the three phenolic rings making dihedral angles with the phenoxide oxygen atoms mean plane of 45(5), 62(1) and 40(4)° (averaged over molecules A and B). The remainder of the macrocycle in **5** is buckled away in such a manner that the mean plane of the atoms O(3), O(4) and O(5) is nearly orthogonal to that of the donor oxygen atoms O(1), O(2), O(6) and O(7) (86.7(2)° in A, 89.9(2)° in B). Here, there is an obvious analogy with the mononuclear uranyl ion complex of *p*-*tert*-butylcalix[7]arene,[9e] in which a tetraphenolic subunit binds the cation and the residual triphenolic unit is bent away so that the dihedral angle between the O_4 and O_3 planes is 90.5(4)°. Complex **5** is, however, completely unlike the uranium(VI) complex formed by *p*-benzylcalix[7]arene,[9f] which is in fact a hexanuclear, polyuranate species where each of the two macrocyclic ligands

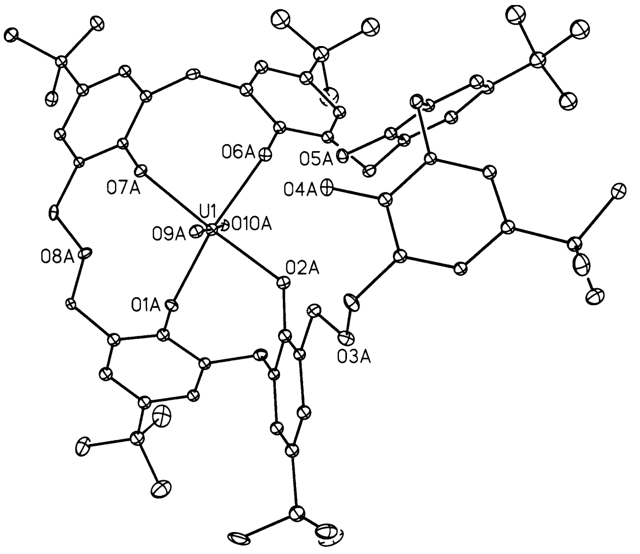

Fig. 2 View of the unit $[UO_2(\mathbf{1} - 4H)]^{2-}$ in complex **5** (molecule A). Hydrogen atoms omitted for clarity. Only the main component of disordered parts is represented.

involved encompasses two metal units, restrictions of the ligand size seemingly leading to the unsymmetrical U=O(uranyl)–U bridge between them, rather than a bridge formed by an additional oxo- or hydroxo-ligand, as found for example in *p*-*tert*-butylcalix[8]arene complexes.[9a,b,g,h] The lesser number of phenolic groups in **1** may explain why any such form for a uranium(VI) complex could be unfavourable, and the parallel with the behaviour of *p*-*tert*-butylcalix[7]arene is also only partial in the sense that in **5** the four donor atoms are drawn from both the tetra- and di-phenolic units rather than just the tetraphenolic unit. **1** may be considered as too large for involving all its donor groups in complexing one uranyl ion and too small for accepting two cations. This point will be further discussed later. O···O distances in **5** (Table 2) indicate hydrogen bonding between O(4) and O(5) and O(5) and O(6), and the two triethylammonium ions are hydrogen-bound to separate sites, one to the uranyl oxygen atom O(10) and the other to the phenoxide one O(7). The former $HNEt_3^+$ species is also included in the cavity formed by the aromatic rings bound to O(1), O(6) and O(7) and the latter in that formed by the rings attached to O(2), O(4) and O(5) of a neighbouring molecule.

With fewer phenolic but more ether oxygen donors, the ligand *p*-methyloctahomotetraoxacalix[4]arene **2** behaves quite differently towards U^{VI}. In the presence of pyridine as a base in place of triethylamine it gives the binuclear complex $[C_5H_5NH][(UO_2)_2(\mathbf{2} - 4H)(OH)(H_2O)]\cdot 2.5C_5H_5N$ **6**, represented in Fig. 3, the monoanionic complex core being close to C_{2v} symmetry. Although each uranium forms bonds to two phenoxide oxygen atoms with normal bond lengths (mean value 2.25(2) Å), an unexpected feature of this structure is the binding of one ether oxygen atom to each, which is observed for the first time in this family of compounds, the coordination geometry of U becoming pentagonal bipyramidal, rather than octahedral as in **5**. The corresponding U–O(ether) bond lengths are long [mean value 2.67(2) Å], with respect to U–O(phenoxide) [mean value 2.24(4) Å in complexes previously characterized[7–10]], U–O(phenol) [mean value 2.54(7) Å] and also U–O(ether) in "internal", six-coordinated, crown ether complexes (2.50–2.58 Å),[9b] suggesting weak interactions, perhaps as a consequence of the nature of the other donors and/or conformational restrictions of the ligand. The two bridges are different, the U–O distance being smaller for O(13) [mean value 2.337(4) Å] than for O(14) [2.497(7) Å] and, conversely, the U–O–U angle being larger [114.7(3) against 104.0(3)°]. These data are consistent with the hypothesis that O(13) corresponds to a hydroxide ion and O(14) to a water molecule [usual values for U–O bond lengths are 2.21(6) Å for O^{2-} bridges,[9f] 2.36(3) Å for (OH^-)[9a,b] and a typical value for H_2O is 2.43 Å]. In turn, this leads to the assignment of one of the four pyridine entities in the asymmetric unit, corresponding to N(1), as being protonated (consistent with its involvement in a hydrogen bond to the ether oxygen atom O(8) and possibly to the uranyl oxygen atom O(12), as shown in Fig. 3b). This pyridine molecule is also included in the calixarene cavity. The two other ones [N(2) and N(3)] are hydrogen bound to the bridging atoms O(13) and O(14), respectively. The previous hypothesis on the nature of these bridging atoms implies that these two pyridine molecules are neutral (another possibility, which seems inconsistent with the geometrical considerations above, would be to suppose the bridges to be O^{2-} and OH^- and all three pyridine molecules to be protonated). The last pyridine molecule is disordered around a symmetry centre and not bound. The equatorial environment of each uranyl ion is a puckered plane, the out-of-plane displacements with respect to the mean planes defined by the five donor atoms (rms deviation 0.30 Å in both cases) being 0.134(3) and 0.117(3) Å for U(1) and U(2), respectively. The dihedral angle between these two planes, which intersect along O(13)···O(14), is 38.2(2)°, comparable to the value of 34(1)° for the corresponding angle

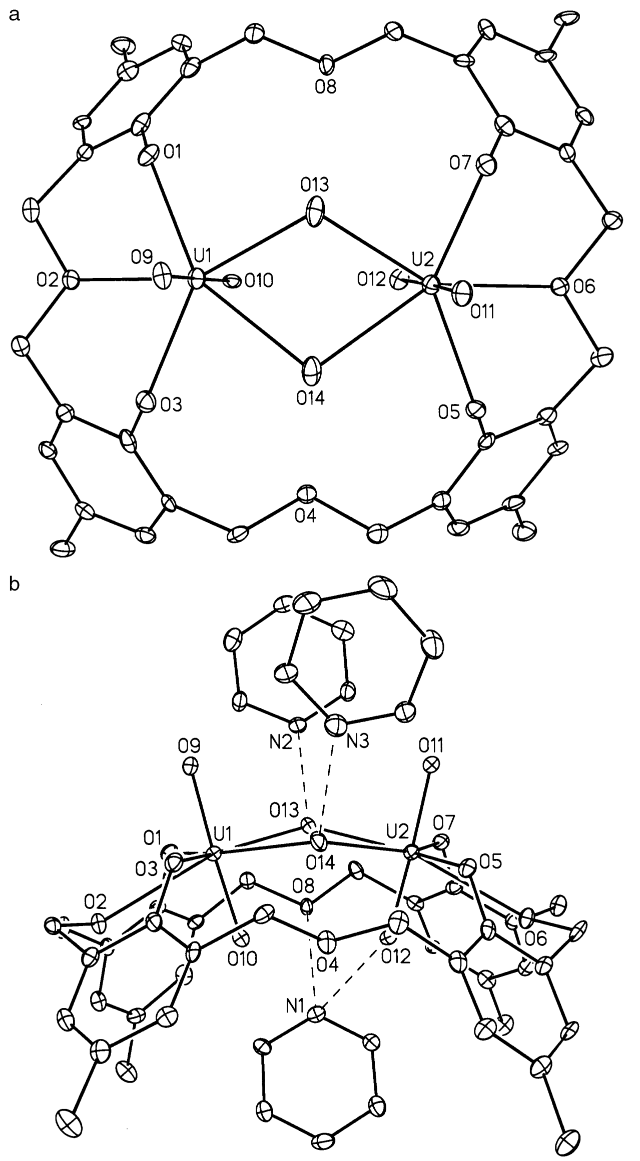

Fig. 3 Two views of the unit $[C_5H_5NH][(UO_2)_2(\mathbf{2} - 4H)(OH)(H_2O)]\cdot 2C_5H_5N$ in complex **6**. (a) Pyridine molecules and hydrogen atoms omitted for clarity. (b) View showing the location of pyridine molecules. Hydrogen bonds as dashed lines. Hydrogen atoms omitted for clarity.

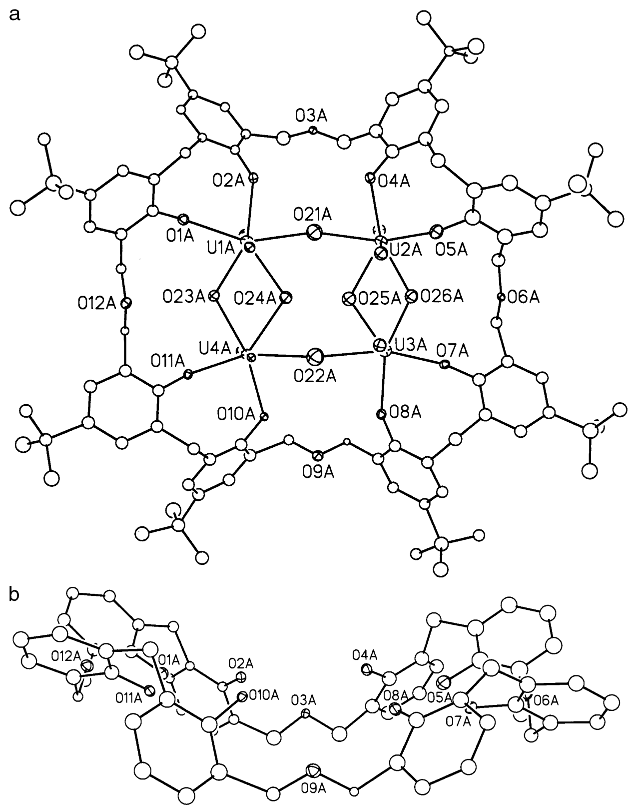

Fig. 4 (a) View of the unit $[(UO_2)_4(\mathbf{3} - 8H)(OH)_2(H_2O)_4]^{2-}$ in complex **7** (molecule A). Only the main component of disordered parts is represented. (b) View of the calixarene alone (molecule A). *tert*-Butyl groups omitted for clarity.

in the binuclear uranyl complexes of *p*-*tert*-butylcalix[8]arene involving a single hydroxide bridge (mean U–O bond length 2.36(3) Å).[9a,b] The calixarene forms a rather deep cone cavity, with the four phenolic rings making dihedral angles of 64.5(2), 50.1(2), 57.5(2) and 52.9(2)° with the mean plane defined by the phenolic oxygen atoms O(1), O(3), O(5) and O(7) (rms deviation 0.08 Å). *p*-*tert*-Butyltetrahomodioxacalix[4]arene ([3.1.3.1]homooxacalixarene), with but two diametrically located ether bridges, has previously been reported to give a mononuclear uranyl complex[10] and, as will be discussed later, has a cavity size insufficiently large for the inclusion of two uranyl ions. The enlargement in **2** by the introduction of two more ether bridges provides sufficient space for two cations, but enforces the unusual ether oxygen coordination.

The uranyl complex $[HNEt_3]_2[(UO_2)_4(\mathbf{3} - 8H)(OH)_2(H_2O)_4]\cdot 1.5NEt_3\cdot 2.5H_2O\cdot CH_3OH$ **7**, derived from *p*-*tert*-butyloctahomotetraoxacalix[8]arene **3**, has only been obtained as low quality single crystals, resulting in a somewhat unsatisfactory crystal structure determination. However, the novelty and interesting nature of this compound justify a description of the gross features of its structure. As seen for one of the two independent but nearly identical molecules found in the asymmetric unit (Fig. 4a), **7** contains a tetranuclear uranate species of a hitherto unknown form. Four uranyl cations are held within the macrocycle by bonding to all eight phenoxide units and are also linked by two single (sb in the following) and two double (db) bridges involving hydroxide and water ligands. Though bond length and bond angle values are imprecise and disperse (Table 2, in which the U–O bond lengths only are reported), consideration of mean values enables some tentative conclusions to be drawn. The presence of two triethylammonium cations and complete deprotonation of the phenolic groups means a total charge of −2 must be associated with the bridging entities, leading to interpretation of the geometrical parameters as consistent with the presence of two double bridges of the same form as that in **6**, *i.e.* as involving one hydroxide and one water each. The bridge adjacent to the calixarene framework or "exterior" (dbe) has the shorter U–O distance and larger U–O–U angle and is thus assigned to hydroxide, leaving the "interior" bridge (dbi) to water. Bond lengths for the singly bridging entities indicate they are also water molecules, though the U–O–U angles differ significantly from those for the water molecule bridges in the doubly bridged units. Hydrogen bonding to the triethylammonium ions differentiates the two molecules of the asymmetric unit, since in A it involves two uranyl oxygen atoms, whereas in B it involves one phenoxide and one uranyl oxygen atom. The various solvent molecules form an extensive hydrogen bound array also involving phenoxide groups. The four O=U=O uranyl axes are not parallel and the mean equatorial coordination planes define dihedral angles of 10(6) and 14(4)° as the mean values for planes linked by single and double bridges, respectively, smaller than in the bimetallic complexes of *p*-*tert*-butylcalix[8]arene. The U · · · U distances are different by about 0.88 Å between sb and db (Table 2), the corresponding distance in the *p*-*tert*-butylcalix[8]arene complexes being intermediate between them [4.501(3) Å], which is consistent with the single OH^- bridge in the latter corresponding to a bond weaker than that of db and stronger than that of the water molecule in sb. Another tetrametallic uranyl complex has recently been reported, in which the ligand is *p*-*tert*-butylcalix[12]arene.[19] This calixarene is slightly larger than the present one and the metallic core is composed of two distinct bimetallic parts, each of them bound to four phenoxide and one phenol oxygen atoms, one pyridine molecule and a doubly chelating nitrate ion. This latter complex, with its polyuranate species smaller than that in **7**, is nearer to the bimetallic complexes of *p*-*tert*-butylcalix[8 and 9]arenes.[9g,h] The conformation of ligand **3** in **7** can unfortunately not be compared to that of its uncomplexed form, no single crystal of the latter having been obtained. If one disregards the ether bridges, the eight phenolic rings have the same orientation as in the complexed *p*-*tert*-butylcalix[8]arene, *i.e.* (uudduudd), in the notation proposed by Kanamathareddy and Gutsche.[20] However, taking the bridges into account, this conformation can be described more accurately as [ud(b)-du(b)ud(b)du(b)], in which (b) stands for the ether bridges. The four ether oxygen atoms are not identically located with respect to the mean plane of the molecule defined by the eight phenolic oxygen atoms (rms deviation 0.13 Å): O(6) and O(12) are slightly displaced on one side [mean distance 0.3(2) Å] whereas O(3) and O(9) are more strongly displaced on the other side [1.7(1) Å], which gives the molecule a curved shape apparent on Fig. 4b. Complex **7** (and in a less obvious manner **6**) provides a new example of complexation of an oligouranyl, or polyuranate, cluster by a calixarene in a basic medium, previously encountered with *p*-*tert*-butylcalix[8]arene (three uranyl ions)[9g,h] and *p*-benzylcalix[7]arene (six uranyl ions for two calixarene molecules).[9f] Analogous cases have been described with rare-earth metal ions, and the calixarenes have consequently been described as potential "cluster keepers".[9g,h]

All the results gathered up to now in the field of uranyl complexes of calixarenes and homooxacalixarenes[9h] enable some conclusions to be drawn on the relation between the size of the ligand and the nature (in particular the nuclearity) of the complex. For parent calixarenes, the number of phenolic units can be taken as the indicator of the size. However, a comparison with homooxacalixarenes necessitates another parameter be considered. The sum of the number of phenolic units and number of ether links, denoted s in the following, appears as a natural and useful parameter, as well as the number of bonds encircling the central ring (which comprises a contribution of 2 for each phenol unit or methylene bridge and 4 for each ether bridge and is equal to $4s$ in the case of classical calixarenes), denoted m. Both numbers give only a rough estimate of the size available for the cation, since the number of

Table 3 Nature of uranyl complexes as a function of calixarene size

Ligand[a]	s	m	Nuclearity	Characteristics of the complex	Reference
Calix[4]arene	4	16		No “internal” complex formed	9(*h*)
Hexahomotrioxacalix[3]arene	6	18	1	Pseudo-trigonal coordination	8
Dihomooxacalix[4]arene	5	18	1	“Square planar” coordination	7
Calix[5]arene	5	20	1	Pentagonal coordination	9(*d*)
Tetrahomodioxacalix[4]arene	6	20	1	“Square planar” coordination	10
Calix[6]arene	6	24		No “internal” complex formed	9(*c*)
Octahomotetraoxacalix[4]arene **2**	8	24	2	Pentagonal coordination	This work
Calix[7]arene	7	28	1	“Square planar” coordination	9(*e*)
			2[b]	Direct uranyl–uranyl bonding	9(*f*)
Tetrahomodioxacalix[6]arene **1**	8	28	1	“Square planar” coordination	This work
Calix[8]arene	8	32	2[b]	Pentagonal coordination	9(*a*),(*b*),(*g*)
Calix[9]arene	9	36	2	Pentagonal coordination	9(*g*),(*h*)
Octahomotetraoxacalix[8]arene **3**	12	40	4	Pentagonal coordination	This work
Calix[12]arene	12	48	4	Pentagonal coordination, two dimers	19

[a] *p*-Substituents omitted. [b] Only uranyl ions located inside the calixarene cavity are taken into account.

phenolic oxygen donor atoms occupying part of the central cavity should obviously also be taken into account. Another drawback is that both parameters do not give any information about the possible geometrical arrangements of the donor atoms. However, some general trends, which may bear some relevance to predict the behaviour of a given ligand, can be deduced from such considerations. Table 3 summarizes the information available (the nuclearity given concerns only the cations located inside the calixarene cavity, *i.e.* bound to more than two phenol/phenoxide groups; the “external” cations or complexes are not considered further, the present classification being irrelevant in this case). Note that 18-crown-6, which is able to hold one uranyl ion bound to all six ether oxygen atoms,[9b] has a s value of 6 and a m value of 18, similar to those of the smallest calixarenes giving 1 : 1 uranyl complexes.

One of the limitations of the present considerations is that slight changes in preparative conditions or ligand substituents may lead to the isolation of very different solid state species, as seen with calix[7]arenes, so that any relation to energy minima for solution species is most uncertain. The influence of conformational preferences for the ligand is also difficult to establish, though certainly the differences in structures of compounds **4** and **5** suggest there would be a marked energy difference between the conformations of the “free” and bound ligand in this case. Furthermore, the necessity to take also into account the number of phenolic donor groups is exemplified by the case of calix[6]arene and octahomotetraoxacalix[4]arene, which present the same value for the parameter m, but behave completely differently, the former giving only “external” complexes and the latter an “internal”, binuclear, one. In this case, the parameter s, which is higher for the latter, is more relevant. For the same m parameter, homooxacalixarenes are clearly more spacious than calixarenes, which is mainly due to a reduction in the amount of space occupied by phenolic oxygen atoms. The comparison between the two ligands dihomooxacalix[4]arene and calix[5]arene, both able to involve all their phenolic groups to complex one uranyl ion, and of ligands **2** and calix[8]arene, both well adapted for holding two bridged uranyl ions in their cavity, indicates that s is also a better choice in those cases, which shows that the replacement of an ether oxygen atom by a phenolic group, in terms of cavity space occupation, is roughly compensated by the size increase corresponding to two units in the m value. The homooxacalixarene **1** possesses the same s value as calix[8]arene and **2**, and it may thus appear as a potential ditopic ligand, under experimental conditions different from those used during the synthesis of complex **5**. The imperfect size-match between ligand and cation in **5** results in a strong ligand distortion. Ligand **3** obviously belongs to the category of “large” calixarenes including more than two cations. Its size somewhat lower than that of calix[12]arene results in a more compact arrangement of the four uranyl ions included, with a bridging of all the cations, by contrast with the double binuclear species in the complex of the latter (the values of s are identical, but the very different conformations in these cases might play an important role). On the basis of limited known work, calix[9]arene appears able to include two uranyl cations but then leaves three phenolic units unbound,[9g,h] in a manner reminiscent of the mononuclear complex of calix[7]arene and of complex **5**, and the inclusion of three uranyl ions in its cavity, under appropriate conditions, cannot be ruled out. The investigation of calix[10]arene and of homooxacalixarenes of similar size is of particular interest in the light of the present discussion, those ligands being at the border between the bi-, tri- and tetra-nuclear cases. Calix[11]arene is seemingly well suited for holding four uranyl ions, more closely packed than in calix[12]arene.

A survey of the crystal structures involving discrete polyuranate species from the October 2000 release of the Cambridge Structural Database System[21] yields relatively few examples of high nuclearity assemblies. A molecular species containing eight uranyl ions is built in fact from four bis(carboxylato)-bridged $[(UO_2)_2(\mu\text{-}O_2)]$ species.[22] A nuclearity of six is obtained by bridging two $[(UO_2)_3(\mu_3\text{-}O)]$ units by two μ-azido-*N*,*N* moieties,[23] whereas it is also observed in the complex of *p*-benzylcalix[7]arene cited above,[9f] in which the uranyl cations are either directly bound one to the other, or bridged by μ-phenoxo or μ_3-oxo units. More examples exist for tetrauranate species, in which a usual central core is $[(UO_2)_4(\mu_3\text{-}O)_2]$ (encountered also in the *p*-benzylcalix[7]arene complex), completed by various monodentate or polydentate and bridging species,[24] but which can also arise from arrangements involving bridging ligands, μ_3-oxo ions and direct uranyl–uranyl oxo bonding.[25] A recent example has also been given of a tetrameric uranyl complex involving alkoxide ligands, some of them bridging, and uranyl–uranyl oxo bonding.[26] Among complexes of trimeric uranyl units, the $[(UO_2)_3(\mu_3\text{-}O)]$ unit is encountered,[27] along with uranyl–uranyl oxo bonding.[28] A discrete trimeric carbonato complex, in which the three cations are held together by doubly bridging carbonate ions, has also been described.[29] In view of these results, it appears that the polyuranate arrangements described in the present work are unprecedented (as well as other ones in calixarene chemistry[9h]) and that “medium” or “large” calixarenes and homooxacalixarenes ($s \geqslant 8$, $m \geqslant 24$) could provide ligands suitable for complexing polynuclear species of desired nuclearity, with a size range and versatility unavailable with any other macrocyclic family. The mechanism of formation of such cluster complexes would deserve an investigation which largely exceeds the scope of the present work. In particular, the characterization of the oxo-linked clusters present in solution would be necessary to know if the calixarene chooses a particular polymetallic species which preexists in solution or if it promotes the formation of a convenient assembly, *i.e.* if the calixarenes are to be considered as "cluster keepers" or as "cluster builders".

Acknowledgements

We particularly thank one referee for a careful critical reading of the manuscript and fruitful comments and suggestions.

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