

Trigonal *versus* tetragonal or pentagonal coordination of the uranyl ion by hexahomotrioxacalix[3]arenes: solid state and solution investigations

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The effects of different substituents and basic agents on the crystal structure of the uranyl complexes of fully deprotonated *p*-R-hexahomotrioxacalix[3]arene have been investigated. The trigonal equatorial coordination previously observed with R = *tert*-butyl and NEt₃ or DABCO as deprotonating agents, and also with H₂NBu as reported herein, appears to be changed to distorted tetragonal coordination in the cases R = methyl and NEt₃ or R = *tert*-butyl and NPr₃ or to distorted pentagonal coordination for R = *tert*-butyl and 4-methylpiperidine, passing through an intermediate case with R = *tert*-butyl and HNBU₂. The rare trigonal uranyl coordination observed in these compounds is likely the result of a subtle equilibrium between electronic and steric factors, the macrocyclic effect probably playing a major role, and it can be easily modified by any perturbation of these factors. Stable complexes could be investigated by ¹H NMR on dissolving the crystals obtained using secondary and tertiary amines in halogenated solvents. Ammonium ion inclusion in the aromatic cavity of an apparently C_{3v} symmetric complex was observed. Although less symmetric forms could not be frozen out at low temperature, the equilibration between two different types of structures was investigated.

Homooxacalixarenes are macrocycles formally derived from calixarenes by replacement of one or more methylene links by CH₂OCH₂ ether links.¹ In the past few years, we have extended an investigation, initiated by Harrowfield *et al.*,² of the uranyl-complexing properties of these macrocycles.³ The complexing properties of simple calixarenes towards this ion have also been extensively studied, particularly from a structural viewpoint, following the demonstration of the 'uranophilic' properties of several members of this family of ligands,⁴ and uranyl might now be considered as a probe permitting the comparison of the complexing preferences of different calixarenes. One of the most interesting and surprising results obtained with homooxacalixarenes is the first evidence of an equatorial trigonal coordination for the uranyl ion (or trigonal bipyramidal coordination for uranium, the oxo ligands occupying the axial positions),^{3a} which has been observed with *p*-*tert*-butylhexahomotrioxacalix[3]arene (compound **2** in Chart 1). Such a coordination mode has not been encountered with classical calixarenes (the smallest calixarene to complex the uranyl ion, calix[4]arene, gives an 'external' complex⁵) and it seems to be a specificity of compound **2**, large enough to complex uranyl in an 'internal' mode and possessing a pseudo-trigonal geometry with two very different groups of potential oxygen donors, phenoxides and ethers, the latter being feebly coordinating and not bound in this case. A second example of a trigonal uranyl geometry, involving amido ligands, has been reported,⁶ which shows that this phenomenon, though previously unobserved, is more than a mere curiosity.

The uranyl-complexing properties of calixarenes and in particular the structural features of the complexes have been shown in some cases to be strongly dependent on the experimental conditions used.^{4b} The nature of the basic agent necessary to deprotonate the phenolic oxygen atoms may be a critical parameter, but limited changes have been made and the effects are badly understood.⁷ So, it appeared interesting to investigate the effect of different bases in the particular case of *p*-*tert*-butylhexahomotrioxacalix[3]arene, which has a unique complexing behaviour. The two bases used in the first study, triethylamine (NEt₃) and 1,4-diazabicyclo[2.2.2]octane (DABCO) gave nearly identical complexes, differing mainly by the hydrogen bonding pattern. The crystal structures of the

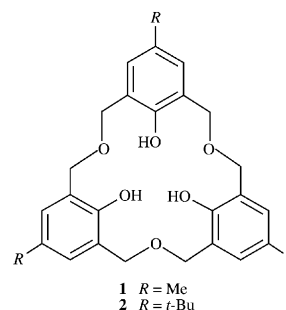


Chart 1 The *para*-substituted hexahomotrioxacalix[3]arenes under study.

complexes obtained with tripropylamine (NPr_3), butylamine (H_2NBu), dibutylamine (HNBu_2) and 4-methylpiperidine (MePi) are reported herein, as well as the structure of the complex obtained with *p*-methylhexahomotrioxacalix[3]arene **1** and triethylamine. Although NMR spectra of calixarene complexes of the uranyl ion in solution have been reported previously, the availability of the present series of closely related species provided an opportunity for an especially thorough investigation.

Experimental

Synthesis

1 and **2** were synthesized as reported in the literature.^{8,9}

[HNEt₃][UO₂(1–3H)] 3. Triethylamine (200 mg, 2.0 mmol) was added dropwise to a boiling, stirred mixture of **1** (32 mg, 0.071 mmol) and uranyl acetate dihydrate (32 mg, 0.075 mmol) in MeOH (10 mL). Stirring and heating of the resulting bright orange solution were continued for an additional 5 min. Dark orange to red single crystals suitable for X-ray crystallography deposited within a few days. Anal. calc. for $\text{C}_{33}\text{H}_{43}\text{NO}_8\text{U}$: C, 48.35; H, 5.29; N, 1.71. Found: C, 48.28; H, 5.33; N, 1.83%.

[HNPr₃][UO₂(2–3H)] · MeOH 4. This compound was prepared on a larger scale. Tripropylamine (500 mg, 3.5 mmol) was added dropwise to a boiling, stirred mixture of **2** (290 mg, 0.50 mmol) and uranyl acetate dihydrate (220 mg, 0.52 mmol) in MeOH (18 mL). The mixture was heated and stirred for an additional 5 min and the dark orange single crystals that deposited upon standing were collected after 4 days (320 mg, 63% yield). Anal. calc. for $\text{C}_{46}\text{H}_{71}\text{NO}_9\text{U}$: C, 54.16; H, 7.02; N, 1.37. Found: C, 53.79; H, 7.18; N, 1.44%.

[H₃NBu][UO₂(2–3H)] 5. This compound was synthesized with the same procedure as **3**, from **2** and butylamine. Anal. calc. for $\text{C}_{40}\text{H}_{57}\text{NO}_8\text{U}$: C, 52.34; H, 6.26; N, 1.53. Found: C, 52.53; H, 6.60; N, 1.83%.

[H₂NBu₂][UO₂(2–3H)] · MeOH 6. This compound was synthesized with the same procedure as **3**, from **2** and dibutylamine. Single crystals suitable for X-ray crystallography deposited within 20 days. Anal. calc. for $\text{C}_{45}\text{H}_{69}\text{NO}_9\text{U}$: C, 53.72; H, 6.91; N, 1.39. Found: C, 54.04; H, 7.01; N, 1.47%.

[HMePi][UO₂(2–3H)] · 2MeOH · H₂O 7. This compound was synthesized with the same procedure as **3**, from **2** and 4-methylpiperidine. Anal. calc. for $\text{C}_{44}\text{H}_{69}\text{NO}_{11}\text{U}$: C, 51.51; H, 6.78; N, 1.37. Found: C, 51.95; H, 6.44; N, 1.49%.

Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer¹⁰ using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The crystals were introduced in glass capillaries with a protecting 'Paratone' oil (Exxon Chemical Ltd.) coating. The unit cell parameters were determined from ten frames, then refined on all data. A 180° φ -range was scanned with 2° steps during data collection, with a crystal-to-detector distance fixed to 28 mm. The data were processed with DENZO-SMN.¹¹ The structures were solved by direct methods (compounds **3**, **5**, **6** and **7**) or Patterson map interpretation (**4**) with SHELXS-97¹² and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.¹³ Absorption effects were corrected empirically with the program DELABS from PLATON.¹⁴

Crystal data and structure refinement parameters are given in Table 1.† The molecular plots were drawn with SHELXTL.¹⁵ All calculations were performed on a Silicon Graphics R5000 workstation.

CCDC reference numbers 172883–172887. See <http://www.rsc.org/suppdata/nj/b108947c/> for crystallographic data in CIF or other electronic format.

NMR measurements

¹H NMR spectra were taken on a Bruker AC 300 spectrometer. CD₂Cl₂ and CDCl₃ were stored over activated molecular sieves (4 Å) and care was taken to minimize exposure to adventitious water during sample preparation. The spectra at low temperatures in CD₂Cl₂ were taken on 4 mmol dm^{−3} solutions and calibrated on the signal of CHDCl₂ at $\delta = 5.32$, whereas 1.5 mmol dm^{−3} solutions and TMS as an internal standard were used in experiments in CDCl₃ at 298 K. A sample of 4% CH₃OH in CH₃OD was used to calibrate the temperature.

Results and discussion

Complexes in the solid state

The first complex, [HNEt₃][UO₂(1–3H)] **3**, differs from one of the complexes previously described, **8**,^{3a} by the replacement of the *p*-*tert*-butyl substituents by *p*-methyl ones, the same base (NEt₃) being used in both cases (a second compound with DABCO as a base, **9**, was also reported). This difference is sufficient to promote some modifications of the bonding pattern, as shown in Fig. 1. Whereas none of the three ether oxygen atoms is bound to the uranium atom in **8**, one of them [O(2)] is coordinated in **3**, giving an overall tetragonal uranyl environment, with a non-crystallographic symmetry plane containing the cation and the coordinated ether atom, instead of a trigonal axis. This environment is much distorted with respect to the quasi-regular square planar environments sometimes observed in calixarene and homooxacalixarene complexes,^{3b,4b,5} since the mean value of the U–O(phenoxide) bond lengths is 2.219(7) Å, whereas the U–O(2) bond length, 2.744(3) Å, indicates a much weaker interaction (Table 2) [the O–U–O angles involving successive oxygen atoms in the plane are also very far from 90°]. The U–O(2) bond length is larger than the only other U–O(ether) bond length reported up to now in a homooxacalixarene uranyl complex, which is 2.67(2) Å,^{3c} and also

† Details of the crystal structure refinements. Some *tert*-butyl groups are disordered in compounds **4**, **5** and **7**, as well as methanol (**4**) or water (**7**) solvent molecules. In compound **4**, one arm of each ammonium cation is disordered around the symmetry plane. The butylammonium ion in compound **5** is disordered over two positions related by the symmetry plane (which contains the nitrogen atom) and one of its carbon atoms is further disordered over two sites. The 4-methylpiperidinium ion in compound **7** is badly resolved and probably disordered around the symmetry plane and it has been refined with constraints on bond lengths and displacement parameters. Ammonium protons were introduced as found on the Fourier-difference maps for compounds **3**, **4** and **6**, as well as the hydroxy protons of methanol molecules in the latter compound. In **5**, owing to the disorder of the ammonium ion, the two protons located in the symmetry plane only were found and introduced. The protons bound to nitrogen and the hydroxy proton of the methanol and water molecules were not found in **7**. All other hydrogen atoms were introduced at calculated positions, except in the disordered parts when present. All hydrogen atoms were treated as riding atoms with a displacement parameter equal to 1.2 (OH, NH, CH, CH₂) or 1.5 (CH₃) times that of the parent atom. All non-hydrogen atoms were refined anisotropically, except the disordered ones in **4**.

Table 1 Crystal data and structure refinement details

	3	4	5	6	7
Empirical formula	C ₃₃ H ₄₃ NO ₈ U	C ₄₆ H ₇₁ NO ₉ U	C ₄₀ H ₅₇ NO ₈ U	C ₄₅ H ₆₉ NO ₉ U	C ₄₄ H ₆₉ NO ₁₁ U
<i>M</i> /g mol ^{−1}	819.71	1020.07	917.92	1006.04	1026.03
<i>T</i> /K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>Pbca</i>	<i>P2₁/m</i>	<i>Pnma</i>	<i>P2₁/c</i>	<i>Pnma</i>
<i>a</i> /Å	16.3031(6)	14.0317(7)	8.8676(4)	25.2169(6)	19.3226(7)
<i>b</i> /Å	19.6564(8)	21.9727(14)	17.6548(11)	16.5010(5)	16.4355(7)
<i>c</i> /Å	19.6680(8)	16.3246(7)	26.4488(14)	24.4065(7)	14.1831(5)
β /°	90	106.837(3)	90	112.739(2)	90
<i>V</i> /Å ³	6302.8(4)	4817.4(4)	4140.7(4)	9366.3(4)	4504.2(3)
<i>Z</i>	8	4	4	8	4
μ /mm ^{−1}	5.202	3.420	3.968	3.517	3.661
Reflections collected	41 417	16 508	26 957	63 517	29 971
Independent reflections	5961	8591	4042	17 694	4428
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	4467	5895	3181	12 894	3042
<i>R</i> _{int}	0.079	0.052	0.117	0.082	0.098
<i>R</i> ₁	0.030	0.057	0.058	0.043	0.047
<i>wR</i> ₂	0.052	0.136	0.149	0.086	0.116

than the bond lengths in six-coordinated crown ether uranyl complexes [2.50–2.58 Å].¹⁶ A search of the Cambridge Structural Database¹⁷ for uranyl–ether bonds gives a mean U–O bond length of 2.43(5) Å for the most common THF coordi-

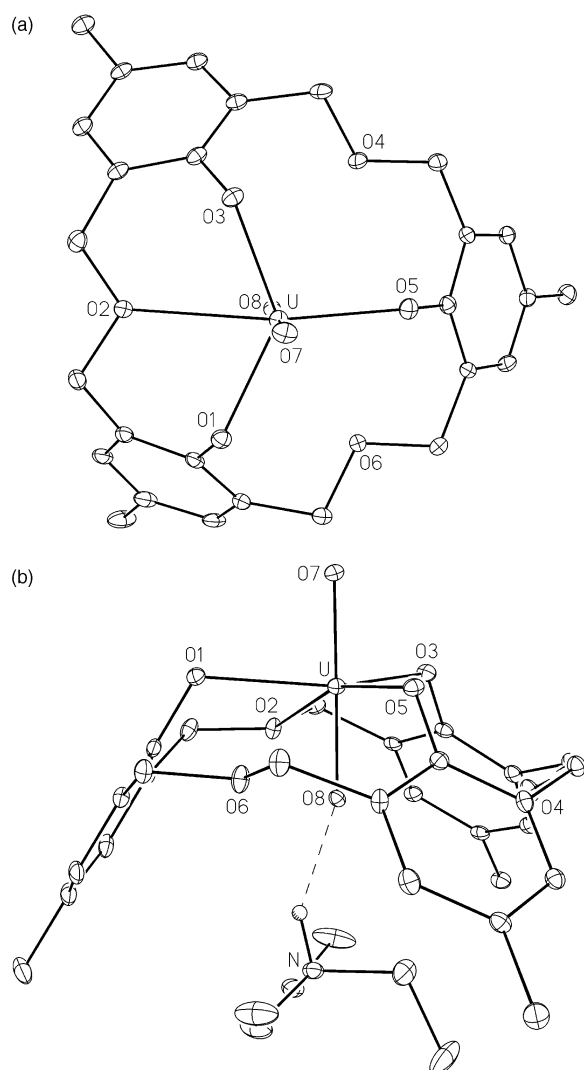


Fig. 1 Two views of the complex [HNEt₃][UO₂(1-3H)] **3**. (a) Counter-ion and hydrogen atoms omitted for clarity. (b) Hydrogen bond as dashed line. Ammonium proton represented as a small sphere of arbitrary radius. Other hydrogen atoms omitted for clarity.

nation and values within the range indicated above for the other cases. For the sake of clarity, it is necessary to fix an upper limit to such U–O(ether) bond lengths, while keeping in mind the continuous range uniting clear-cut coordination bonds to weak interactions. We shall consider in the following that a bond occurs when the condition used in SHELXTL¹⁵ is met, *i.e.* when the interatomic distance is less than the sum of the covalent radii plus an additional factor fixed to 0.5 Å (2.96 Å for U–O bonds), which is, of course, a rather arbitrary choice and may include weak interactions. The U–O(2) bond length in **3** meets this condition, but obviously cannot be considered as a strong coordination bond, probably due to the geometric constraints arising from the macrocyclic nature of the ligand. Furthermore, the uranyl environment in **3** is far from being perfectly equatorial: the uranium atom is located at 0.128(2) Å from the mean plane defined by the three phenoxide oxygen atoms, denoted O₃ in the following (a value slightly lower than those in **8** and **9**), but the ether atom O(2) is at 1.026(5) Å from this plane (Table 3). The other two ether atoms O(4) and O(6) are at even larger distances from this mean plane and their distance towards uranium indicates their non-coordinating character (Table 2). The conformation of the ether bridge varies significantly upon coordination of the central oxygen atom. All the bridges in the uranyl complexes of **1** and **2** characterized up to now correspond to *anti* C–O–C–C(arom) torsion angles, which results in quasi-planar, ‘w’-shaped, bridges.¹⁸ However, if the distance between the central oxygen atom and the mean plane C₄ defined by the four carbon atoms around it (which deviates from planarity by less than 0.05 Å in compound **3**, as for all the other compounds reported herein) is considered, it appears that the coordination of O(2) is accompanied by a significant departure from planarity (Table 3). By contrast to the non-coordinating ether atoms, the coordinated one is displaced on one side of the bridge so as to come closer to uranium and to direct its lone pairs in an appropriate way. The homooxalixarene in **3** is in the cone conformation, as in compounds **8** and **9**. Some parameters permitting a closer comparison between the complexes under study are reported in Table 3. The distances between the phenoxide oxygen atoms are larger than those between phenol oxygen atoms in the uncomplexed macrocycle **2** [3.03(5) Å]¹⁹ and are comparable to those in compounds **8** and **9** [3.80(8) Å]. However, the O(1)···O(3) distance is significantly larger than the two other ones, which is due to the presence of O(2) in the coordination sphere [as reflected also in the O(1)–U–O(3) angle being larger than the other ones]. It may be noted that the U···O(ether), O(ether)···O₃ and O(phenoxide)···O(phenoxide) distances and the O(phenoxide)–U–O(phenoxide) angle are correlated:

Table 2 Environment of the uranium atom in compounds **3–7**: selected distances (Å) and angles (°)

	U–O(oxo)		U–O(phenoxide)		U–O(ether)		O–U–O	
3	U–O(7)	1.789(3)	U–O(1)	2.227(3)	U–O(2)	2.744(3)	O(7)–U–O(8)	179.4(1)
	U–O(8)	1.790(3)	U–O(3)	2.218(3)	U...O(4)	3.478(3)	O(1)–U–O(2)	69.1(1)
			U–O(5)	2.213(3)	U...O(6)	3.056(3)	O(2)–U–O(3)	69.3(1)
							O(1)–U–O(3)	132.8(1)
							O(3)–U–O(5)	105.8(1)
4							O(5)–U–O(1)	120.4(1)
	U(1)–O(5A)	1.788(9)	U(1)–O(1A)	2.261(7)	U(1)...O(2A)	3.313(6)	O(5A)–U(1)–O(6A)	177.6(4)
	U(1)–O(6A)	1.773(7)	U(1)–O(3A)	2.233(6)	U(1)–O(4A)	2.681(8)	O(1A)–U(1)–O(3A)	111.6(2)
							O(3A)–U(1)–O(4A)	70.3(2)
							O(3A)–U(1)–O(3A')	135.3(3)
	U(2)–O(5B)	1.770(9)	U(2)–O(1B)	2.256(7)	U(2)...O(2B)	3.369(7)	O(5B)–U(2)–O(6B)	177.2(4)
	U(2)–O(6B)	1.763(7)	U(2)–O(3B)	2.216(8)	U(2)–O(4B)	2.636(9)	O(1B)–U(2)–O(3B)	110.0(2)
							O(3B)–U(2)–O(4B)	71.6(2)
							O(3B)–U(2)–O(3B')	138.8(4)
							O(5)–U–O(6)	179.6(3)
5	U–O(5)	1.799(9)	U–O(1)	2.186(7)	U...O(2)	3.022(8)	O(1)–U–O(3)	125.7(1)
	U–O(6)	1.791(7)	U–O(3)	2.205(5)	U...O(4)	3.534(7)	O(3)–U–O(3')	107.5(3)
6	U(1)–O(7A)	1.776(4)	U(1)–O(1A)	2.260(4)	U(1)–O(2A)	2.950(4)	O(7A)–U(1)–O(8A)	179.7(2)
	U(1)–O(8A)	1.788(4)	U(1)–O(3A)	2.206(4)	U(1)...O(4A)	3.286(4)	O(1A)–U(1)–O(2A)	65.9(1)
			U(1)–O(5A)	2.220(4)	U(1)...O(6A)	3.017(4)	O(2A)–U(1)–O(3A)	67.3(1)
							O(1A)–U(1)–O(3A)	123.1(2)
							O(3A)–U(1)–O(5A)	113.8(2)
							O(5A)–U(1)–O(1A)	120.4(2)
	U(2)–O(7B)	1.785(4)	U(2)–O(1B)	2.264(4)	U(2)–O(2B)	2.927(4)	O(7B)–U(2)–O(8B)	179.5(2)
	U(2)–O(8B)	1.780(4)	U(2)–O(3B)	2.214(4)	U(2)...O(4B)	3.197(5)	O(1B)–U(2)–O(2B)	65.8(1)
			U(2)–O(5B)	2.196(4)	U(2)...O(6B)	3.040(4)	O(2B)–U(2)–O(3B)	67.1(1)
							O(1B)–U(2)–O(3B)	123.5(2)
							O(3B)–U(2)–O(5B)	115.3(2)
							O(5B)–U(2)–O(1B)	118.4(2)
							O(5)–U–O(6)	176.6(3)
							O(1)–U–O(2)	67.0(1)
							O(2)–U–O(3)	69.2(2)
7	U–O(5)	1.776(7)	U–O(1)	2.240(7)	U–O(2)	2.818(6)	O(1)–U–O(3)	127.8(1)
	U–O(6)	1.790(7)	U–O(3)	2.236(5)	U...O(4)	3.716(7)	O(3)–U–O(3')	102.4(3)

Symmetry code: ' = $x, 0.5 - y, z$.

O(6) is closer to uranium and to the mean plane than O(4), which may indicate some kind of interaction with the cation, and, accordingly, the O(1)...O(5) distance and O(1)–U–O(5) angle are larger than their counterparts involving O(3) and O(5). As in compounds **8** and **9**, the calixarene cavity is deeper than in the uncomplexed compound **2**, with dihedral angles between the aromatic rings and the mean plane O_3 in the range

46.9(1)–59.7(1)° [mean value 37(2)° in **2**¹⁹]. The triethylammonium cation is included in this cavity and forms as usual a hydrogen bond with the oxo atom O(8) (Table 4).

Compound **4**, [HNPr₃][UO₂(**2**–3H)]·MeOH, involves the same ligand as compounds **8** and **9**, but the basic agent used is the bulkier NPr₃. The asymmetric unit comprises two half-molecules, denoted A and B, the pseudo-symmetry plane of

Table 3 Ligand geometry in compounds **3–7**: selected distances (Å) and dihedral angles (°) involving the mean planes; C_4 defined by the carbon atoms of the ether bridges, O_3 defined by the three phenoxide oxygen atoms and the aromatic rings $\phi(i)$ [associated with O(*i*)]

	O(phenoxide)...O(phenoxide)		O(ether)...C ₄		O(ether)...O ₃		$\phi(i)$ – O_3	
3	O(1)...O(3)	4.073(4)	O(2)	0.419(4)	O(2)	1.026(5)	$\phi(1)$	59.7(1)
	O(3)...O(5)	3.534(4)	O(4)	0.121(4)	O(4)	1.726(5)	$\phi(2)$	47.1(1)
	O(1)...O(5)	3.853(4)	O(6)	0.212(4)	O(6)	1.352(5)	$\phi(3)$	46.9(1)
4	O(1A)...O(3A)	3.717(8)	O(2A)	0.011(8)	O(2A)	1.603(8)	$\phi(1A)$	42.5(2)
	O(3A)...O(3A')	4.13(1)	O(4A)	0.48(1)	O(4A)	0.93(1)	$\phi(2A)$	57.0(2)
	O(1B)...O(3B)	3.663(9)	O(2B)	0.024(9)	O(2B)	1.655(9)	$\phi(1B)$	41.8(2)
	O(3B)...O(3B')	4.15(2)	O(4B)	0.50(1)	O(4B)	0.88(1)	$\phi(2B)$	55.2(3)
5	O(1)...O(3)	3.907(8)	O(2)	0.19(1)	O(2)	1.32(1)	$\phi(1)$	54.1(2)
	O(3)...O(3')	3.55(1)	O(4)	0.19(1)	O(4)	1.75(1)	$\phi(2)$	48.6(2)
6	O(1A)...O(3A)	3.927(6)	O(2A)	0.252(5)	O(2A)	1.324(6)	$\phi(1A)$	50.1(1)
	O(3A)...O(5A)	3.708(6)	O(4A)	0.011(6)	O(4A)	1.520(6)	$\phi(2A)$	49.3(2)
	O(1A)...O(5A)	3.889(6)	O(6A)	0.226(6)	O(6A)	1.369(7)	$\phi(3A)$	51.5(2)
	O(1B)...O(3B)	3.945(6)	O(2B)	0.292(6)	O(2B)	1.243(6)	$\phi(1B)$	49.6(1)
	O(3B)...O(5B)	3.724(5)	O(4B)	0.067(6)	O(4B)	1.471(6)	$\phi(2B)$	50.3(2)
	O(1B)...O(5B)	3.830(6)	O(6B)	0.178(6)	O(6B)	1.439(6)	$\phi(3B)$	47.3(2)
7	O(1)...O(3)	4.019(8)	O(2)	0.37(1)	O(2)	1.208(8)	$\phi(1)$	59.4(2)
	O(3)...O(3')	3.49(1)	O(4)	0.27(1)	O(4)	1.73(1)	$\phi(2)$	49.0(2)

Symmetry code: ' = $x, 0.5 - y, z$.

Table 4 Hydrogen bonding geometry in compounds **3–7**: selected distances (Å) and angles (°)

	X...Y		X–H		H...Y		X–H...Y	
3	N...O(8)	2.766(5)	N–H	0.94	H...O(8)	1.92	N–H...O(8)	148.5
4	N(1)...O(1A)	2.78(1)	N(1)–H(1)	1.12	H(1)...O(1A)	1.66	N(1)–H(1)...O(1A)	179.9
	N(2)...O(1B)	2.80(1)	N(2)–H(2)	0.81	H(2)...O(1B)	2.00	N(2)–H(2)...O(1B)	168.8
5	N...O(4)	2.91(1)	N–H(1)	0.89	H(1)...O(4)	2.02	N–H(1)...O(4)	179.6
	N...O(5')	2.79(1)	N–H(2)	0.89	H(2)...O(5')	2.02	N–H(2)...O(5')	144.5
6	N(1A)...O(9A)	2.713(6)	N(1A)–H(1A)	0.76	H(1A)...O(9A)	2.09	N(1A)–H(1A)...O(9A)	138.7
	N(1A)...O(1A'')	2.801(6)	N(1A)–H(2A)	0.75	H(2A)...O(1A'')	2.07	N(1A)–H(2A)...O(1A'')	166.1
	N(1B)...O(9B)	2.732(7)	N(1B)–H(1B)	0.76	H(1B)...O(9B)	1.98	N(1B)–H(1B)...O(9B)	171.2
	N(1B)...O(1B''')	2.827(6)	N(1B)–H(2B)	0.95	H(2B)...O(1B''')	1.90	N(1B)–H(2B)...O(1B''')	163.8
	O(9A)...O(4A)	2.799(6)	O(9A)–H(9A)	0.89	H(9A)...O(4A)	1.92	O(9A)–H(9A)...O(4A)	167.1
	O(9B)...O(4B)	2.754(6)	O(9B)–H(9B)	0.92	H(9B)...O(4B)	1.84	O(9B)–H(9B)...O(4B)	170.0
7^a	N...O(6)	2.79(1)	N...O(8''')	2.84(2)	O(8)...O(1)	2.64(1)	O(8)...O(4''')	2.99(1)

Symmetry codes: ' = $x - 1, y, z$; '' = $-x, y - 0.5, 0.5 - z$; ''' = $1 - x, y + 0.5, 1.5 - z$; '''' = $x + 0.5, y, 0.5 - z$; ''''' = $x - 0.5, y, 0.5 - z$. ^a Hydrogen atoms not found.

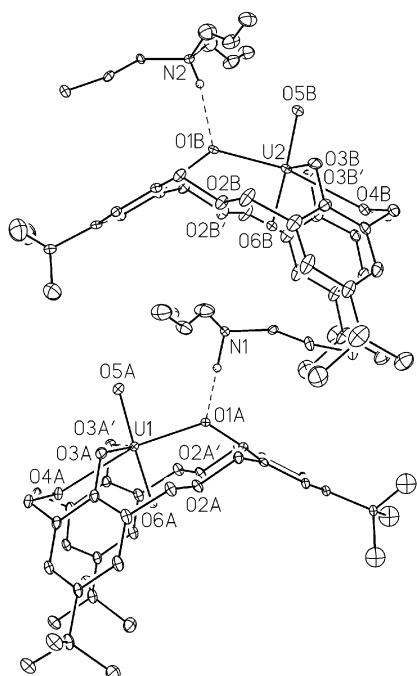


Fig. 2 View of $[\text{HNPr}_3][\text{UO}_2(2-3\text{H})]\cdot\text{MeOH}$ **4**. The two independent molecules A and B are included. Hydrogen bonds as dashed lines. Ammonium protons represented as small spheres of arbitrary radii. Other hydrogen atoms and methanol molecule omitted for clarity.

compound **3** being a crystallographic one in **4** (one *tert*-butyl group and one propyl chain being disordered). In both molecules A and B, the ether oxygen atom O(4), located on the symmetry plane as the phenoxide atom O(1), is coordinated to uranium, with a mean U–O bond length of 2.66(3) Å, slightly shorter than that in **3** but in good agreement with the value of 2.67(2) Å previously found.^{3c} The difference in planarity between the ether bridges associated with O(2) and O(4) is consequently larger [O(4) being as far as *ca.* 0.5 Å from the mean plane C_4] and the O(4)...O₃ distance [mean value 0.91(4) Å] shorter than their counterparts in **3**. The mean value of U–O(phenoxide) bond lengths is 2.24(2) Å. The remarks regarding the details of the calixarene geometry made for compound **3** hold also for compound **4**. The tripropylammonium cations are included in the cavity of each calixarene, but, instead of being hydrogen bonded to an oxo atom, they are linked to the phenoxide oxygen atom O(1) of the neighbouring

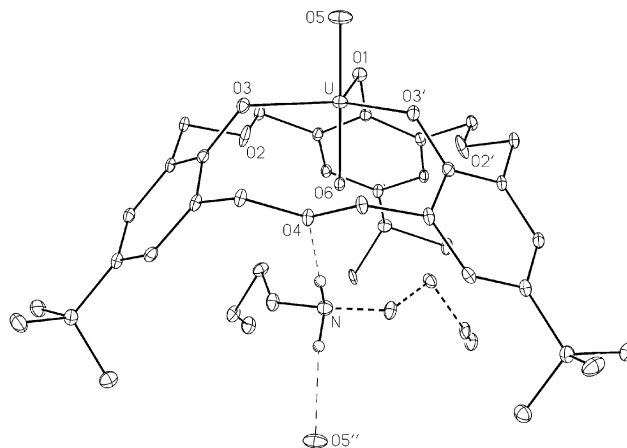


Fig. 3 View of $[\text{H}_3\text{NBu}][\text{UO}_2(2-3\text{H})]$ **5**. One of the two positions of the ammonium *n*-butyl chain is represented in bold dashed lines. Hydrogen bonds as dashed lines. Ammonium protons represented as small spheres of arbitrary radii (third proton not found). Other hydrogen atoms omitted for clarity. Symmetry code: ' = $x, 0.5 - y, z$; '' = $x - 1, y, z$.

molecule along the *c* axis, as illustrated in Fig. 2, in a manner similar to that observed, for example, in the *p*-*tert*-butyldihomooxacalix[4]arene uranyl complex.² It appears that the lengthening of the ammonium cation aliphatic chains by one unit results in a different (but hardly predictable) positioning with respect to the calixarene. It is likely that the slight conformational changes induced in the macrocycle in this way, with respect to compounds **8** and **9**, are sufficient to promote the coordination of one ether oxygen atom.

Up to now, tertiary amines only have been used as deprotonating agents. Compound **5**, $[\text{H}_3\text{NBu}][\text{UO}_2(2-3\text{H})]$, involves a primary amine with a longer butyl chain. The resulting complex, represented in Fig. 3, possesses a symmetry plane containing the uranyl ion, the phenoxide oxygen atom O(1) and also the nitrogen atom of the counter-ion, the butyl chain being disordered over two positions. However, the coordination sphere of uranium admits a pseudo-trigonal axis, as in compounds **8** and **9**, the cation being bound to the three phenoxide donors only. The ether oxygen atoms are at distances from uranium larger than 3 Å and the ether bridges are close to planarity. The mean U–O(phenoxide) bond length is 2.20(1) Å, identical to those in compounds **8** and **9** [2.20(3) Å]. Such values in trigonal uranyl complexes appear to be slightly smaller than those in complexes with higher coordination

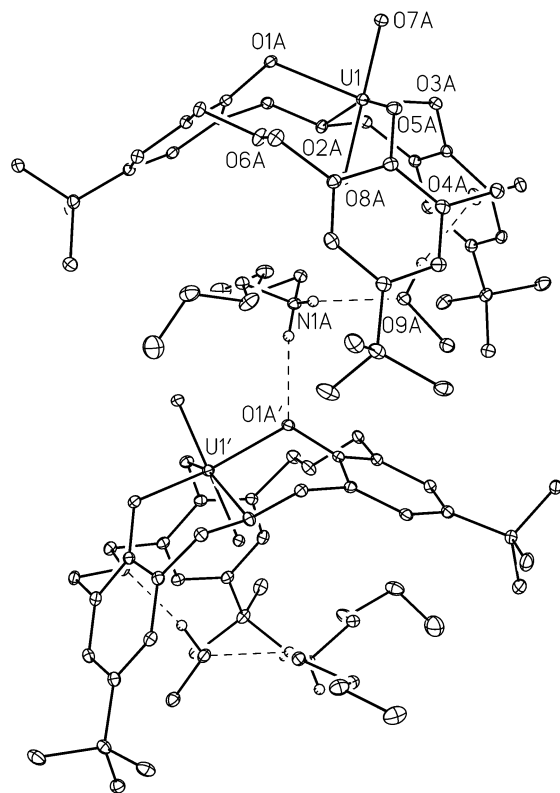


Fig. 4 View of $[\text{H}_2\text{NBu}_2][\text{UO}_2(2-3\text{H})]\cdot\text{MeOH}$ **6**, showing the packing in the case of molecule A. Hydrogen bonds as dashed lines. Ammonium and methanol protons represented as small spheres of arbitrary radii. Other hydrogen atoms omitted for clarity. Symmetry code: $' - x, y - 0.5, 0.5 - z$.

numbers. The mean value for all the four-coordinated complexes of **1** and **2** reported herein is $2.23(2)$ Å, *i.e.* about 0.03 Å larger than the preceding values. Such a reduction of the U–O(phenoxide) bond length in the trigonal complexes, although it can be considered as barely significant, may be an effect of the necessity for the ligand to maximize electron donation in these complexes.⁶ The ammonium cation in **5** is hydrogen bonded to the ether oxygen atom O(4) and to an oxo group of a neighbouring molecule. The first of these two bonds may be thought to contribute to preventing O(4) from being bound to the uranyl cation. However, the absence of such bonds for the other ether oxygen atoms in compound **5** as well as in compounds **8** and **9** do not support this hypothesis.

Compound **6**, $[\text{H}_2\text{NBu}_2][\text{UO}_2(2-3\text{H})]\cdot\text{MeOH}$, involves the corresponding secondary amine, dibutylamine. The asymmetric unit comprises two independent and nearly identical molecules, denoted A and B. Each of them is packed along the *b* axis with its own symmetrically-related molecules, as represented in Fig. 4 in the case of molecule A. As previously observed in the case of the $\text{NEt}_3/\text{NPr}_3$ pair, the replacement of H_2NBu by the bulkier HNBu_2 results in some modifications of the coordination geometry, the ether oxygen atom O(2) being closer to uranium than the other two. However, the U–O(2) bond lengths in both molecules A and B are larger by 0.2 – 0.3 Å than their counterparts involving O(2) in **3** and O(4) in **4**, with a mean value of $2.94(2)$ Å, close to the limit mentioned above, and its distance from the mean plane O_3 is also larger, with a mean value of $1.28(6)$ Å and the question arises as whether to consider such distances as indicative of a true coordinative bond. As in compound **3**, one of the other ether atoms [O(6)] is also closer to uranium than the third. However, the O(phenoxide)···O(phenoxide) distances and the O(phenoxide)–U–O(phenoxide) angles span a narrower range than in compound **3**. All these geometrical features confirm the

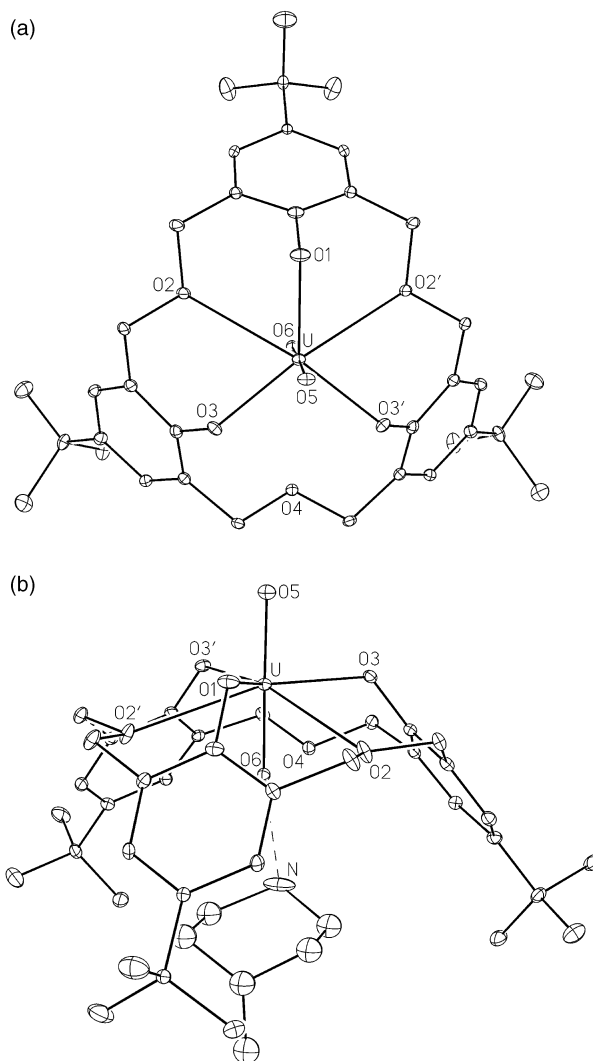


Fig. 5 Two views of $[\text{HMePi}][\text{UO}_2(2-3\text{H})]\cdot 2\text{MeOH}\cdot\text{H}_2\text{O}$ **7**. (a) Counter-ion, solvent molecules and hydrogen atoms omitted for clarity. (b) Hydrogen bond as dashed line. Hydrogen atoms and solvent molecules omitted for clarity.

borderline nature of this complex, which may be considered as intermediate between trigonal and distorted tetragonal uranyl coordinations. The ammonium cation is included in the calixarene cavity as usual, but a new feature appears with the simultaneous inclusion of a methanol molecule. The hydrogen bonding pattern is modified, since the ammonium cation is bound to one phenoxide oxygen atom of the neighbouring molecule along the *b* axis and also to the methanol oxygen atom O(9). The latter is in its turn hydrogen bonded to the ether oxygen atom O(4). The ability of protonated secondary or primary amines to give hydrogen bonded polymers, as illustrated in compounds **5** and **6**, is a trend that could be exploited in the design of supramolecular systems.

A more clear-cut case in what concerns uranyl coordination is encountered when the cyclic secondary amine 4-methylpiperidine is used as a base, resulting in the compound $[\text{HMePi}][\text{UO}_2(2-3\text{H})]\cdot 2\text{MeOH}\cdot\text{H}_2\text{O}$ **7**, Fig. 5. The asymmetric unit comprises half a molecule, with the symmetry plane containing the uranyl moiety, the phenolic oxygen atom O(1), the ether oxygen atom O(4) and the nitrogen atom of the base. Instead of containing the uranium-bound ether atom as in compound **4**, the symmetry plane in **7** contains a non-coordinating ether. The other ether atom O(2) and its symmetry-related counterpart O(2') are feebly bound to uranyl, with a U–O(2) distance of $2.818(6)$ Å. The O(2)··· O_3 distance

is larger than the corresponding O(2)···O₃ in **3** and O(3)···O₃ **4**, but the difference in the angles O(1)–U–O(3) [127.8(1)°] and O(3)–U–O(3') [102.4(3)°], as well as that in the corresponding O(phenoxide)···O(phenoxide) distances, are clearly related to the introduction of O(2) within the uranium coordination sphere. The environment of uranyl can thus be described as distorted pentagonal. The mean U–O(phenoxide) value, 2.238(3) Å, is not significantly different from that in the tetragonal complexes. In spite of the impossibility to find the hydrogen atoms in this structure, it appears that the ammonium cation is seemingly involved in divergent hydrogen bonds, as in compounds **5** and **6**, being linked to the oxo atom directed towards the macrocycle cavity and to the oxygen atom O(8) of a disordered water molecule, which is hydrogen bonded itself to the phenoxide and ether atoms O(1) and O(4) of neighbouring macrocycles. The axial position of the methyl substituent in the included cation should be noted.

The present results confirm that the ether oxygen atoms of hexahomotrioxacalix[3]arenes can be found to be coordinated to the uranyl cation, though weakly due to the constrained geometry of the ligand. This had been previously observed only once in the homooxacalixarene family, in the dinuclear uranyl complex of *p*-methyloctahomotetraoxacalix[4]arene,^{3c} in which it was seemingly enforced by the relative narrowness of the macrocycle. Such ether coordination is always observed in the rare-earth ion complexes of **2**.²⁰ In the present case of *p*-R-hexahomotrioxacalix[3]arenes, the question is to determine the factors that promote ether coordination. First of all, it must be noted that the trigonal coordination of uranyl in compounds **8**, **9** and **5** is likely to be far less stable than that in the tris[bis(trimethylsilyl)amido] complex, the latter ligand being a strong σ - and π -donor,⁶ and is certainly mainly stabilized by a macrocyclic effect, the three phenoxide groups being rather rigidly held in the suitable geometry. As a consequence, slight modifications of the species may result in an enlargement of the uranium coordination sphere. In the case of the difference between complexes **3** and **8**, steric and/or electronic effects may be invoked. The methyl groups in ligand **1** are less strong electron-donating groups than the *tert*-butyl groups in ligand **2**. The phenoxide groups in **2** may thus be considered to be somewhat more basic, and hence more coordinating than those in **1**, which may favour ether coordination in the latter case. This effect is certainly small, as suggested by the difference between the *pK_a* values for *p*-methyl- and *p*-*tert*-butyl-phenol, which is only about 0.2. Steric effects may arise from the different *p*-substituent in **3** and, in compounds **4–7**, from the different sizes and geometries of the bases, but such effects may prove impossible to distinguish from packing effects. Moreover, although inclusion of the protonated base in the cavity is a permanent trend, it may be accompanied by co-included solvent molecules as in compound **6**, or the ammonium ion position may vary according to differing hydrogen bonding patterns. As a conclusion, the trigonal coordination of uranyl in these compounds may be viewed as resulting from a subtle equilibrium between

electronic and geometric parameters involving at least two molecular species (the anionic complex and the counter-ion) and easily disrupted by slight perturbations on one or the other.

It may be noted that cation– π interactions apparently play a role in the inclusion of the counter-ion in the aromatic cavity, which has been observed in all cases. The importance of the latter interaction in biological and synthetic systems has been stressed by Dougherty and coworkers who analysed several systems both in crystal form and in solution.²¹ Such interactions have been particularly investigated in solution in the case of quaternary ammonium ions as included in neutral cyclophanes,^{21a,22} for which classical hydrogen bonds and anion–cation interactions are absent. The distances observed in complexes **3–7** between the centroids of the aromatics and the atoms of the included cation appear to be in several cases in the useful range. In particular, the shortest distances between the carbon atoms bound to nitrogen and a centroid are 3.84, 4.01, 3.29, 3.64 and 3.76 Å for complexes **3**, **4**, **5**, **6** and **7**, respectively, to be compared with the value 3.36 Å reported for the crystal structure of the complex between acetylcholine chloride and neutral resorcin[4]arene.²³ Obviously in the present case the cation interacts with an overall anionic species and separation of the various contributions is uncertain.²⁴

Complexes in solution

¹H NMR spectra of the complexes **3–7** in dilute CDCl₃ solution at 298 K are shown in Fig. 6. The spectra of **3**, **4**, **6** and **7** are consistent with the formation of complexes in which the ligand is in an enforced *cone* conformation, namely in these cases one AX system is observed for geminally-coupled CH₂OCH₂ protons, with signals at δ = 4.4 and 6.0. On the other hand, in the case of **5** the singlet signal of the free ligand at δ = 4.72 prevails over the small signals of the AX system. The other signals in the spectra are consistent with extensive complex dissociation only in the case of compound **5**. Besides being split, the signals of the CH₂OCH₂ protons appear to be shifted downfield by 0.4–0.5 ppm with respect to those of the free ligands. Complex formation has a striking effect on the ¹H NMR signals of the ammonium counter-ion, which are all found at high fields. In order to assess this effect, spectra of triethylammonium, tripropylammonium, dibutylammonium and 4-methylpiperidinium tetrafluoroborate were taken in the same conditions. The upfield shift observed for the signals of the several protons of the counter-ion on complex formation is reported in Fig. 7. In all cases the effects are very strong and consistent with the inclusion of the ammonium ion in the aromatic cavity.^{21a,22,25} The shielding effect of the aromatic clouds appears to be stronger the closer the proton to the charged nitrogen, except in the case of the 4-methylpiperidinium ion in complex **7**. Actually, an ambiguity exists in the latter case because chair inversion can be superimposed on the inclusion effect, as suggested by the crystal structure in which

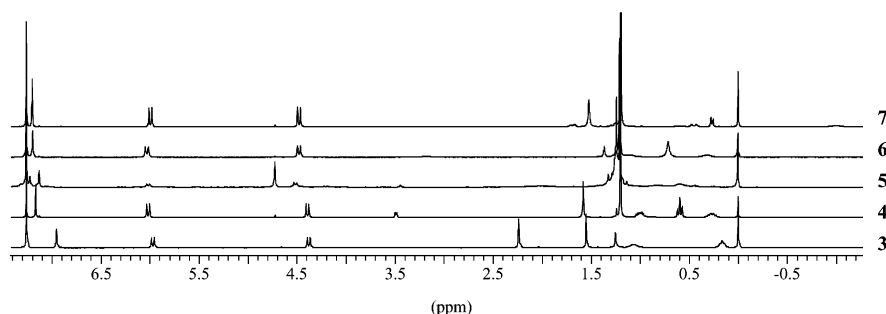


Fig. 6 ¹H NMR spectra of complexes **3–7**, 1.5 mmol dm^{−3} solutions in CDCl₃ at 298 K.

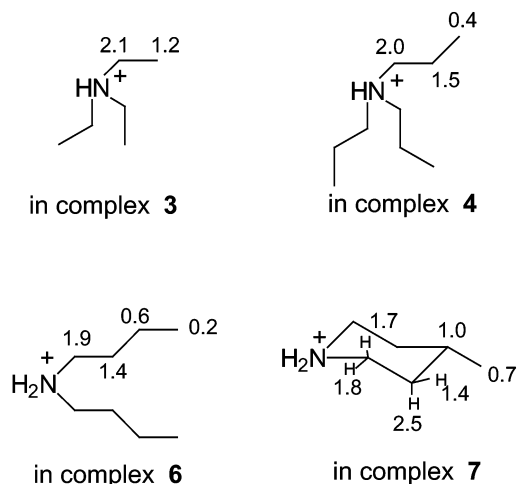


Fig. 7 Upfield shifts for the protons of the ammonium cation on uranyl complex formation (CDCl_3 , 298 K). Equatorial methyl conformation has been assumed for CH_2 protons in the 4-methylpiperidinium ion, in both the reference salt and in compound 7.

the methyl substituent is found to be in an axial position. Interestingly, complex formation between simple ligand **2** and several quaternary ammonium ions takes place in CDCl_3 solution and can be quantitatively analysed through the shielding effects on the included cation.²⁶ The signal of the methyl protons of CH_3OH could not be detected at all in the spectrum of **7** and appeared to be partly broadened but hardly shifted in the case of **6**, whereas it was found unchanged in its standard position at $\delta = 3.49$ in the case of **4**. So the solvent is probably somehow retained in the complex in solution in the case of **7** but is probably lost in the case of **4**. No signal splitting for the diastereotopic geminal protons of the ammonium ion is evident in the spectra of **3**, **4** and **6**. Most importantly, the spectra in Fig. 6 indicate C_{3v} symmetric complexes for the anionic moiety, in spite of the varying coordination observed in the crystals. The apparent symmetry in solution can be due to fast equilibration, on the NMR timescale, between less symmetric species, and an attempt was made to freeze such forms through low temperature experiments in CD_2Cl_2 solution. The results of such an experiment in the case of **3** are shown in Fig. 8. Signal splitting takes place at low temperature but not according to what is expected for distorted tetragonal or distorted trigonal complexes. Two apparently C_{3v} symmetric forms appear to be in equilibrium, each one featuring singlet signals for ArH and ArMe protons, one AX system for the CH_2OCH_2 protons and the two expected signals for coupled protons of the triethylammonium ion. The relative stability of the two forms markedly changes with temperature, a clear-cut inversion being observed between 193 and 213 K. The chemical shifts of the triethylammonium moiety suggest that the inclusion of the

counter-ion dramatically changes between the two forms, the strong upfield shifts being only observed for the form favoured at high temperature (form I). In the case of the low temperature form (form II) the upfield shifts relative to uncomplexed triethylammonium tetrafluoroborate are only 0.4 and 0.2 ppm for methyl and methylene protons, respectively. From a qualitative point of view the same picture holds also for complexes **4**, **6** and **7**, but the relative stability of the two forms at a given temperature changes within the series. Although only rough estimates of the relative abundance of forms I and II could be made in several cases, clear-cut trends are apparent in Fig. 9, in which preliminary results for **8** are also reported. Obviously, peak coalescence limits the useful temperature range for this study, but on extrapolating the observed trends all the complexes are expected to be almost completely in form I at room temperature. Three families can be distinguished from the trends apparent in Fig. 9, with the relative stability of the form I decreasing in the order $4 > 8 \approx 3 > 6 = 7$. Form I thus appears to be favoured by tertiary more than by secondary ammonium ions and by tripropylammonium more than by triethylammonium ions.

Summing up, on cooling the CD_2Cl_2 solutions the interconversion between two forms of complexes can be investigated. The existence of tetracoordinated or penta-coordinated structures, or simply of distorted trigonal structures, for uranyl complexes of hexahomotrioxacalix[3]arenes in solution is not confirmed by the present study but probably the interconversion between less symmetric forms is still rapid at the lowest temperature attained, namely 183 K. Fast chain rotation apparently occurs for the ammonium cation in compounds **3**, **4** and **6** since no difference is apparent for geminal protons, and nor for the two or three carbon chains. Even if the detailed coordination mode as observed in the crystal could not be confirmed in solution, the gross features of stable uranyl complexes in the enforced *cone* conformation and ammonium cation inclusion in the aromatic cavity have been checked to be present for complexes obtained from secondary and tertiary amines. The inclusion of butylammonium ion is also evident for the fraction of undissociated complex in the case of **5**, although signal broadening prevented precise signal assignment in this case.

The substantial exit of the counter-ion from the cavity upon cooling is an interesting feature. The change in the counter-ion position is probably related to changes in hydrogen bonding patterns and to the relative importance of cation- π interactions on changing the temperature. The observed trend $4 > 8 \approx 3 > 6 = 7$ apparently corresponds to decreasing bulkiness around nitrogen atoms and increasing ease of formation of hydrogen bonds. Such crystal structures as those of **4** and **6** feature interesting polymeric arrays with ammonium ions externally hydrogen bonded to the homooxacalixarene but entering the cavity of neighbouring homooxacalixarene units. Such polymeric structures are likely to be peculiar to the crystal state and are probably broken in diluted solution. In the monomeric complex in solution, limiting cases can be envisaged

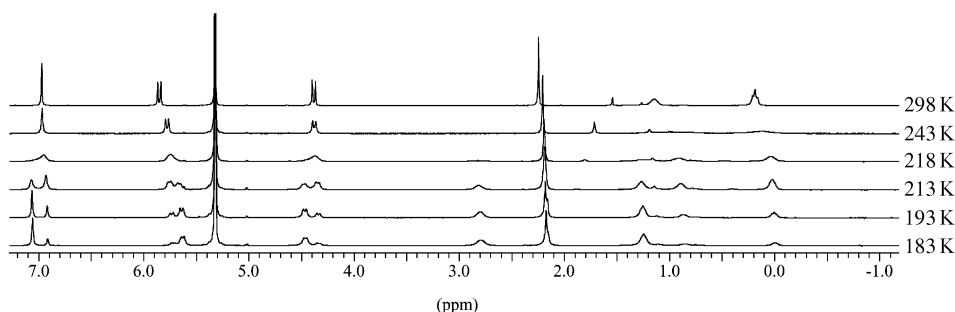


Fig. 8 ¹H NMR spectra of complex **3** at various temperatures in CD_2Cl_2 .

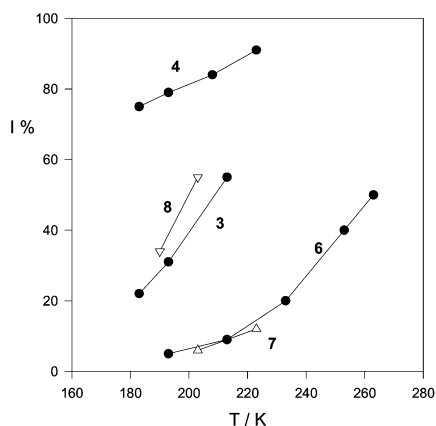


Fig. 9 Effect of temperature on the relative abundance of the complex form I, featuring a well-included ammonium ion.

featuring (i) external hydrogen bonded ammonium ion, (ii) internal non-hydrogen bonded ammonium ion, and (iii) internal (rotated) hydrogen bonded ammonium ion. Arrangement (iii) should benefit from both hydrogen bonding and cation- π interaction but oxygen phenoxide atoms are expected to be stronger hydrogen bond acceptors so that the external complex (i) could possibly be the most stable form at low temperature. It is suggested that the observed forms I and II of the complexes correspond in general to the supposed limiting forms (iii) and (i), respectively. Fast equilibration between different forms (iii) is required to observe highly symmetric complexes in the spectra and, on the other hand, the closeness of the cation to the aromatic ring of the externally hydrogen bonded phenoxide can account for the relatively small shielding effects observed in the case of forms II.

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