DALTON
FULL PAPER

Complexation of uranyl ions by polyphenols. Crystal structures of two linear oligomers and one uranyl ion complex

Pierre Thuéry,*[a] Martine Nierlich,[a] Zouhair Asfari[b] and Jacques Vicens[b]

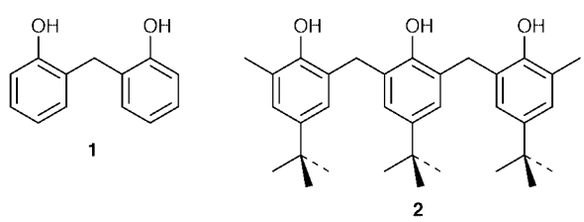
[a] *CEA/Saclay, SCM (CNRS URA 331), Bât. 125, 91191 Gif-sur-Yvette, France. E-mail: thuery@drecam.cea.fr*
[b] *ECPM, Laboratoire de Chimie des Interactions Moléculaires Spécifiques (CNRS UMR 7512), 25 rue Becquerel, 67087 Strasbourg, France*

Received 4th February 2000, Accepted 22nd February 2000
Published on the Web 29th March 2000

The crystal structures of two acyclic phenolic oligomers with *ortho*-methylene linkages, possessing two (**1**) or three (**2**) phenolic units, have been determined. Compound **1** crystallizes with DABCO (1,4-diazabicyclo[2.2.2]octane) and water molecules, with which it forms hydrogen bonds, and is not deprotonated by the basic agent; **2**, which is analogous to half a *p-tert*-butylcalix[6]arene, crystallizes as a cyclic dimer, with hydrogen bonds between the terminal phenolic units of both molecules. In the presence of DABCO, **2** is doubly deprotonated and forms a complex with uranyl ions, in which two triphenol molecules encompass the cation, each of them bonded by two consecutive phenolate oxygen atoms only. Two protonated DABCO molecules form hydrogen bonds with the two uranyl oxygen atoms. The bidentate nature of **2** in this complex is discussed in relation with previous results with calixarenes as ligands.

Following the work of Harrowfield and his group, we have been interested during recent years in the crystal structures of complexes of the uranyl ion UO_2^{2+} with calixarenes and homooxacalixarenes.[1] These ligands, when deprotonated with basic agents such as triethylamine or DABCO (1,4-diazabicyclo[2.2.2]octane), are able to provide the equatorial environment suitable for uranyl ions, with four or five donor atoms in the general case (an exceptional environment with three donor atoms has recently been reported[1h]). During the course of this work we also obtained a binuclear complex of uranyl with an acyclic six-membered phenolic oligomer, which is the acyclic analogue of *p-tert*-butylcalix[6]arene.[2] In this complex each uranyl ion is bonded to three phenolic oxygen atoms, two of which are deprotonated, the co-ordination environment being completed by a bis-chelating nitrate ion. The overall geometry observed is close to that in the binuclear uranyl complex of *p-tert*-butylcalix[8]arene,[1b,c,i] in which the bis-chelating nitrate ion is replaced by two phenolic oxygen atoms and one bridging hydroxyl ion. Apart from an increased 'flattening' in the polyphenol, the conformations of the two ligand molecules are very similar. This similarity holds true also with the binuclear uranyl complex of *p-tert*-butylcalix[9]arene.[1i] This result, which indicated the interest of polyphenols for uranyl complexation, in particular for comparison purposes with the analogous calixarene complexes, led us to investigate the complexes of lower-order oligomers, such as the di- and triphenols which are the subject of the present study (Scheme 1). The use of triethylamine as a deprotonating agent during uranyl complexation did not enable us to grow single crystals from the solutions, notwithstanding the colour change (from yellow to dark orange) which indicated that the reaction occurred. Only with DABCO, the interest in which has been pointed out previously,[1g,h] we were able to obtain the uranyl complex of the triphenol **2** described here.

Linear phenolic oligomers with two to four units and various types of substituents have been the subject of some structural work,[3] which evidenced their particular tendency to organize in dimers or chains by intermolecular hydrogen bonding and also their ability to complex neutral organic molecules. The crystal structures of metal ion complexes of bidentate diphenols have also been described,[4] but, to the best of our knowledge, no complex involving a polyphenol with more than two units has been reported to date, apart from the uranyl complex of a hexaphenol already mentioned.[2]



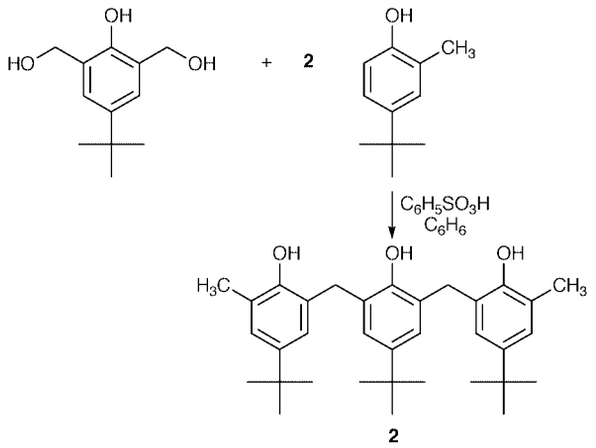
Scheme 1 The phenolic oligomers studied.

Experimental

Synthesis

Diphenol **1** was purchased from Aldrich and used without further purification. When **1** (1.7 mmol) was treated with uranyl nitrate hexahydrate (1 mmol) in the presence of an excess of DABCO (5 mmol) in methanol (200 ml) the solution became dark orange, indicating at least a partial uranyl complexation. However, colourless single crystals of **1**·0.5DABCO·0.5H_2O **3** only were obtained.

Triphenol **2** was prepared according to Scheme 2. 4-*tert*-Butyl-2,6-dihydroxymethylphenol (26 mmol), 4-*tert*-butyl-2-methylphenol (83 mmol) and a catalytic amount of benzenesulfonic acid (1 mmol) were dissolved in 30 ml of benzene and stirred for two hours. A precipitate deposited, which was filtered off and washed with hexane to yield pure triphenol **2** (6.02 g, 11 mmol; 42% yield) as a white solid (mp 190–191 °C). ^{1}H NMR (200 MHz, $CDCl_3$, $SiMe_4$): δ 7.18 (s, 4 H, H aromatic), 6.98 (s, 2 H, H aromatic), 5.54 (br s, 3 H, OH), 3.90 (s, 4 H, $ArCH_2Ar$), 2.23 (s, 6 H, CH_3) and 1.28 (s, 27 H, C_4H_9). Calc. for $C_{34}H_{46}O_3$: C, 81.23; H, 9.22. Found: C, 81.43; H, 9.10%. Recrystallization of **2** from nitromethane



Scheme 2 Synthesis of triphenol **2**.

gave colourless single crystals of **2**·CH_3NO_2 (**4**) suitable for X-ray crystallography.

$(UO_2^{2+})(2 - 2H)_2(HDABCO^+)_2 \cdot CH_3OH$ 5. Triphenol **2** (0.5 mmol) was dissolved in methanol (100 ml) and an excess of 1,4-diazabicyclo[2.2.2]octane (DABCO, ≈4 mmol) was added. A solution of uranyl nitrate hexahydrate (0.25 mmol) in methanol (30 ml) was then added dropwise, yielding a dark orange solution. Single crystals with the same colour as the solution deposited, which were suitable for X-ray crystallography, in spite of rather low quality. Orange solid (mp 87–88 °C). ^{1}H NMR (200 MHz, $CDCl_3$, $SiMe_4$): δ 9.84 (s, 4 H, ArOH), 7.62 (sharp m, 4 H, U–O–ArH), 7.40 (sharp m, 2 H, U–O–ArH), 7.12 (sharp m, 2 H, H aromatic), 6.98 (sharp m, 2 H, H aromatic), 4.20–3.51 (m, 8 H, $ArCH_2Ar$), 2.31–2.19 (m, 12 H, CH_3) and 1.49–1.12 (m, 54 H, C_4H_9) (the signals relative to the DABCO molecules are not indicated). Microanalysis results, obtained from a mixture of single crystals and microcrystalline powder, were unsatisfactory due to the heterogeneous nature of the latter.

Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer[5] using graphite monochromated Mo-Kα radiation (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 the HKL package.[6] The structures were solved by direct methods with SHELXS 86[7] and subsequent Fourier-difference synthesis and refined by full-matrix least squares on F^2 with SHELXL 93.[8] No absorption correction was done for the organic compounds **3** and **4**. Absorption effects in complex **5** were corrected empirically with the program MULABS from PLATON.[9] The DABCO molecule in **3** is located around a symmetry centre and is disordered over four positions sharing the two nitrogen atoms; these positions have been refined with occupation factors constrained to sum to unity [equal to 0.360(9), 0.312(10), 0.186(9) and 0.142(7)] and some soft restraints on bond distances. Two *tert*-butyl groups in **4** were found disordered and modelled with six terminal carbon atoms with occupancies constrained to sum to unity; some constraints were applied to bond lengths in the badly resolved nitromethane molecule. All non-hydrogen atoms were refined anisotropically in the three structures, except the disordered ones. The hydroxyl protons were found on the Fourier-difference map for **3** and **4** and introduced as riding atoms with a displacement factor equal to 1.2 times that of the parent atom. The hydroxyl protons and those bonded to nitrogen atoms in $HDABCO^+$ ions were not found in **5** due to the rather low quality of the data and the hydrogen bonds were inferred from short O···O and O···N contacts. All other hydrogen atoms were introduced at calculated positions in the three structures (except those of the water molecule in **3** and of the disordered groups in **3** and **4**) 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. Crystal data and structure refinement parameters are given in Table 1. The molecular drawings were done with SHELXTL.[10] All calculations were performed on a Silicon Graphics R5000 workstation.

CCDC reference number 186/1868.

See http://www.rsc.org/suppdata/dt/b0/b001083i/ for crystallographic files in .cif format.

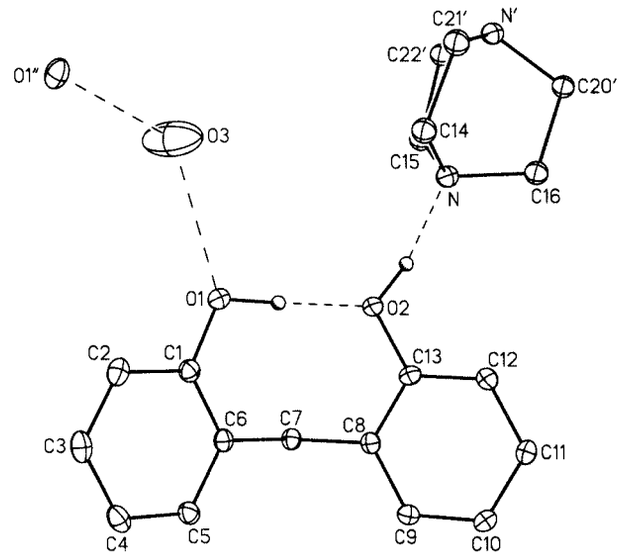


Fig. 1 View of the molecular unit in compound **3**. Hydrogen bonds as dashed lines. Hydroxyl protons represented as small spheres of arbitrary radii. Other hydrogen atoms omitted for clarity. One of the four positions of the DABCO molecule only is represented. Symmetry codes: $' -x, 1 - y, -z$; $'' -x, y, -z - \frac{1}{2}$.

Table 1 Crystal data and structure refinement details for compounds **3**, **4** and complex **5**

	3	**4**	**5**
Empirical formula	$C_{32}H_{38}N_2O_5$	$C_{69}H_{95}NO_8$	$C_{81}H_{118}N_4O_9U$
M	530.64	1066.46	1529.82
T/K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a/Å	25.833(1)	9.6578(4)	17.452(3)
b/Å	7.2184(5)	18.329(2)	17.580(3)
c/Å	17.9962(7)	19.732(2)	17.809(3)
α/°		67.485(3)	64.591(7)
β/°	123.669(3)	77.104(5)	69.983(9)
γ/°		82.634(5)	75.936(10)
V/Å^3	2793(3)	3142(3)	4607(3)
Z	4	2	2
μ/mm^{-1}	0.085	0.072	1.809
Reflections collected	10687	24106	24103
Independent reflections	2466	6147	8939
Observed reflections [$I > 2\sigma(I)$]	1959	4322	6282
R_{int}	0.027	0.106	0.114
$R1$	0.062	0.082	0.094
$wR2$	0.177	0.173	0.217

Results and discussion

The asymmetric unit in compound **3** contains one diphenol molecule, half a DABCO and half a water molecule. The two nitrogen atoms of the DABCO molecule are related to each other by a symmetry centre, whereas the water molecule is located on a binary axis. As indicated in Fig. 1, both intra- and inter-molecular bonds are present (Table 2). The crystal structure of **1** without solvent molecules has previously been

Table 2 Selected bond distances (Å) and angles (°)

Uranium environment in complex **5**					
U–O(1)	2.18(1)	U–O(4)	2.18(1)	U–O(7)	1.81(1)
U–O(2)	2.28(1)	U–O(5)	2.26(1)	U–O(8)	1.83(1)
O(1)–U–O(2)	85.5(4)	O(5)–U–O(4)	84.4(4)	O(7)–U–O(8)	178.6(5)
O(2)–U–O(5)	100.6(4)	O(4)–U–O(1)	89.6(5)		
Hydrogen bonds					
3					
O(1)···O(2)	2.673(2)	H···O(2)	1.646	O(1)–H···O(2)	178.6
O(2)···N	2.605(3)	H···N	1.665	O(2)–H···N	166.9
O(1)···O(3)	2.860(3)				
4					
O(1A)···O(2A)	2.665(4)	H···O(2A)	1.637	O(1A)–H···O(2A)	174.4
O(2A)···O(3A)	2.689(5)	H···O(3A)	1.644	O(2A)–H···O(3A)	166.1
O(3A)···O(1B)	2.654(5)	H···O(1B)	1.553	O(3A)–H···O(1B)	170.9
O(1B)···O(2B)	2.639(6)	H···O(2B)	1.626	O(1B)–H···O(2B)	169.2
O(2B)···O(3B)	2.675(6)	H···O(3B)	1.634	O(2B)–H···O(3B)	171.7
O(3B)···O(1A)	2.684(4)	H···O(1A)	1.572	O(3B)–H···O(1A)	174.5
5					
O(2)···O(3)	2.60(2)	O(6)···O(5)	2.68(1)	O(4)···O(9)	2.77(2)
O(7)···N(3)	2.84(2)	O(8)···N(1)	2.71(1)		

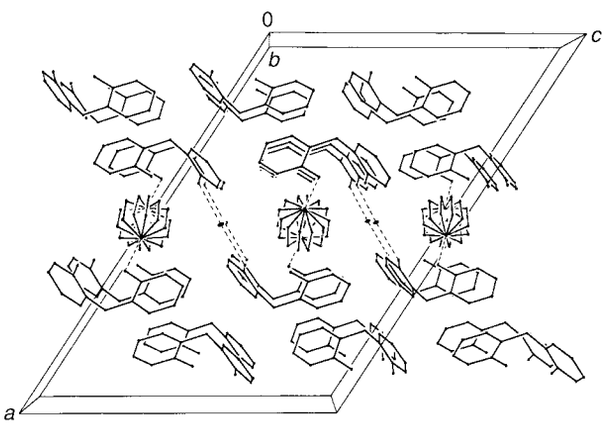


Fig. 2 Crystal packing in compound **3**. The four positions of the disordered DABCO molecules are represented. Hydrogen bonds as dashed lines (intramolecular bonds omitted). For clarity, the DABCO molecules in the forefront only are represented. Hydrogen atoms omitted.

described,[3b] in which intra- and inter-molecular hydrogen bonds give rise to zigzag chains. In **3** each diphenol molecule is bonded to two others by bridging DABCO and water molecules, which gives rise also to zigzag chains directed along the *c* axis (Fig. 2). The protons are located on the two oxygen atoms of **1**, one involved in the intra- and the other in the intermolecular bond. The dihedral angle between the two aromatic rings within the same molecule is 61.81(8)°, which is lower than those observed in the structure of unsolvated **1** and of the uncomplexed diphenols with more or less distorted 'butterfly' conformations previously described, ranging from 74 to 110°.[3b,d,f] Such different values, which are compatible with the existence of intramolecular hydrogen bonds in all cases, are likely due to different intermolecular hydrogen bonds and packing forces and also to the substituents present on the aromatic rings. The torsion angles defining the diphenol conformation, which are usually taken[3a,d] in a similar way as later proposed for calixarenes (torsion angles φ and χ),[11] assume usual values (Table 3). The most prominent feature of the structure lies with the DABCO moiety, which is disordered over four positions sharing the two nitrogen atoms bonded to diphenol molecules. Those positions are nearly equally spaced and their occupation factors not much different. Furthermore, this disorder is identical at room temperature and at 100 K, which indicates its statistical nature. The packing can be viewed as built from bilayers of tail-to-tail diphenol units separated by layers of DABCO and water molecules, all of them parallel to the *bc* plane. The hydrogen bonds assure the cohesion of those two kinds of layers. The previously reported diphenols crystallize as zigzag chains[3b,f] or as cyclic dimers defining $[(O–H)_4]$ rings.[3d] In one case, the formation of chains *via* bridging ethanol molecules has been reported, which bears some similarity with the present structure.[3d] The presence of isodromic hydrogen bonds with formation of infinite chains is known to lead to particularly stable systems.[3b]

Table 3 Conformational parameters φ and χ[11] (°)

		Molecule 1		Molecule 2	
Compound	Rings	φ	χ	φ	χ
3	1–2	−89.8	92.5		
4	1–2	−89.2	92.2	−86.3	93.6
	2–3	87.7	−81.2	81.9	−96.4
5	1–2	84.4	−84.8	73.6	−87.3
	2–3	−90.7	95.7	−87.3	111.5

This compound was obtained during an attempt to synthesize the uranyl complex of **1**. Obviously, by contrast with what is observed with calixarenes,[1g,h] the diphenol in **3** is not deprotonated by DABCO. Although the colour change of the reaction solution indicated at least a partial complexation reaction, the isolation of crystals of **3** in significant quantity suggests that this basic agent is not sufficient to promote a quantitative complexation reaction. This is probably related to the observation of an increased acidity in calixarenes with respect to their acyclic analogues, and also in higher order polyphenols with respect to lower-order ones.[12] It ensues that triphenols may be more suited for uranyl complexation than diphenols.

The crystal structure of the solvated triphenol **4** presents usual features. As illustrated in Fig. 3, the asymmetric unit comprises two hydrogen-bonded molecules forming a cyclic dimer. The conformation of the triphenol molecules is *trans* (or *anti*, with rings 1 and 3 on different sides of the plane defined by ring 2) with the two diphenolic subunits (rings 1,2 and 2,3) in

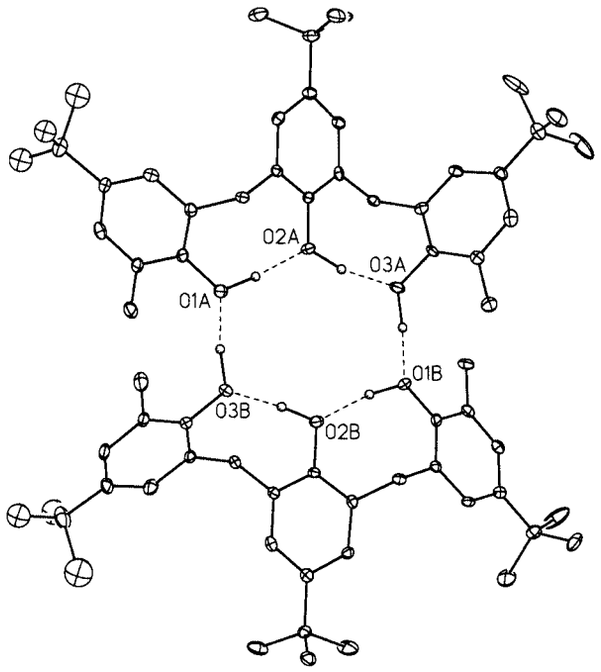


Fig. 3 View of the molecular unit in compound **4**. Hydrogen bonds as dashed lines. Hydroxyl protons represented as small spheres of arbitrary radii. Other hydrogen atoms and solvent molecule omitted for clarity. Only one position of the disordered *tert*-butyl groups is represented.

'butterfly' shape, which is the conformation assumed by half a calix[6]arene in the classical *pinched cone* conformation[11] (whereas a *syn* conformation would give rise to half a *cone* cavity). Four intra- and two inter-molecular hydrogen bonds form a $[(O–H)_6]$ ring, with a mean value of 2.67(2) Å for the O···O distances. The dihedral angles between consecutive aromatic rings are 64.0(2) and 78.3(2)° in molecule A and 72.1(2) and 71.5(1)° in molecule B, which are values lower than those previously reported for analogous conformations.[3a,b,f] The torsion angles φ and χ define a $-++-$ sequence, with values comparable to those in *p-tert*-butylcalix[6]arene.[11] On the whole, the shape of the cyclic dimer is nevertheless different from that of *p-tert*-butylcalix[6]arene, due to the steric hindrance between the terminal methyl groups, which prevents the terminal aromatic rings of the two molecules from coming into closer contact. The structure of the triphenol analogous to **2** less the terminal methyl groups has previously been reported.[3f] In this case the overall shape of the cyclic dimer is nearer to that of *p-tert*-butylcalix[6]arene. The packing in **4** consists in a stacking of cyclic dimers along the *a* axis, the solvent molecule occupying voids between the columns thus formed.

The asymmetric unit in the uranyl complex **5**, with the formula $[(UO_2^{2+})(\mathbf{2} - 2H)_2](HDABCO^+)_2{\cdot}CH_3OH$, contains one uranyl ion, two doubly deprotonated triphenol molecules and two protonated DABCO ions, without any symmetry element. As illustrated in Figs. 4 and 5, the uranyl ion is bonded in its equatorial plane to four phenolic oxygen atoms, which can be stated as deprotonated on the basis of charge equilibrium. The complexing phenolic units of each triphenol molecule are located on different sides of the uranyl equatorial plane, which is never observed in complexes with small calixarenes such as *p-tert*-butyldihomooxacalix[4]arene,[1a] *p-tert*-butylhexahomotrioxacalix[3]arene[1h] or *p-tert*-butylcalix[5]-arene,[1e] in which the cation is at the centre of the lower rim of the calixarene in *cone* conformation, but occurs with higher-order calixarenes[1b,c,g] and also with the acyclic hexaphenol.[2] The two remaining, uncomplexed, phenolic rings in **5** are on the same side of the molecule viewed along the uranyl ion axis but, as it appears in Fig. 5, they are located on different sides of the uranyl equatorial plane. The four U–O distances are not equivalent, those with O(1) and O(4) [2.18(1) Å] being shorter than those with O(2) and O(5) [mean value 2.27(1) Å]. This is likely due to the steric hindrance associated with the uncomplexed phenolic units, which prevents O(2) and O(5) from coming nearer to the uranium atom. As a consequence, the O(2)–U–O(5) angle is the largest of the four angles defining the equatorial co-ordination environment, as well as the O(2)···O(5) distance [3.49(1) Å, to be compared to 2.98(2), 3.03(2) and 3.07(2) Å for the three other O···O distances]. The uranyl ion is nearly perpendicular to the plane defined [within ±0.048(5) Å] by U, O(1), O(2), O(4) and O(5), with a mean O(uranyl)-U–O(phenol) angle value of 90(2)°. The O···O distances suggest the existence of intramolecular hydrogen bonds between the protonated oxygen atoms O(3) and O(6) and their nearest neighbours O(2) and O(5), respectively. Another hydrogen bond exists between O(4) and the oxygen atom O(9) of the solvent methanol molecule. The conformation of the two triphenolic units is *trans*, as in compound **4**. The dihedral angles beween adjacent aromatic rings are 63.4(4) and 74.5(5)° in the first molecule and 67.4(4) and 62.4(4)° in the second molecule. The torsion angles define the same $-++-$ sequence as in **4**,

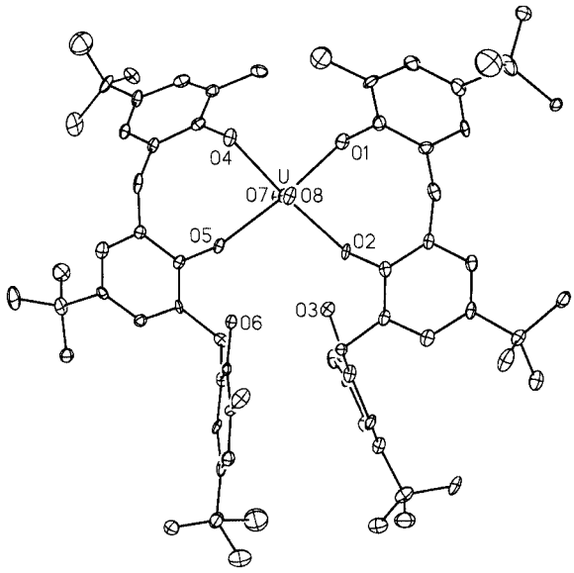


Fig. 4 View of the molecular unit in complex **5**. Hydrogen atoms, counter ions and solvent molecule omitted for clarity.

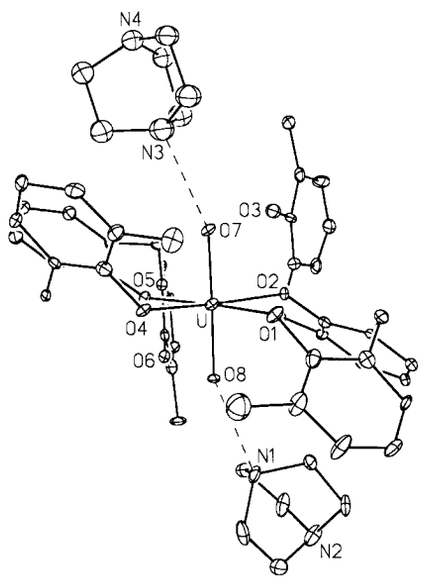


Fig. 5 View of the molecular unit in complex **5** including the counter ions. Hydrogen bonds as dashed lines. Hydrogen atoms, *tert*-butyl groups and solvent molecule omitted for clarity.

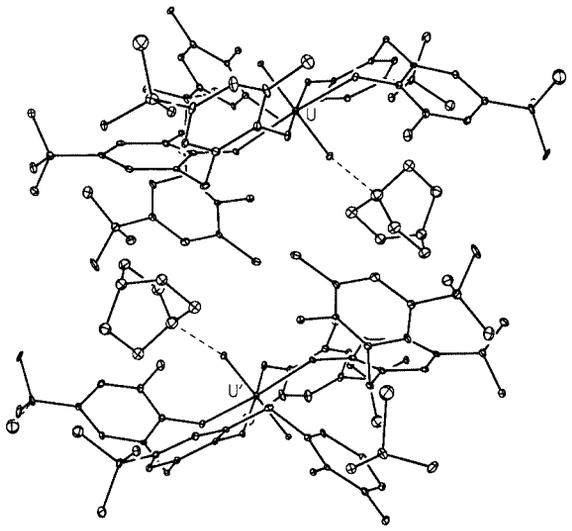


Fig. 6 View of the structure of complex **5** showing the encapsulation of $HDABCO^+$ ions in the cavity formed by two adjacent triphenols. Solvent molecules and hydrogen atoms omitted for clarity.

i.e. the same as in *p-tert*-butylcalix[6]arene. However, it must be noted that, even more than in **4**, the association of the two triphenol molecules in **5** is far from assuming the overall shape of *p-tert*-butylcalix[6]arene. The two $HDABCO^+$ ions are located on each side of the molecule and hydrogen bonded to the uranyl oxygen atoms, as previously observed with this cation or with triethylammonium ions.[1b,c,e–h] The mean O ··· N distance is 2.77(9) Å, which is in agreement with the distances obtained with triethylammonium ions [mean value 2.76(6) Å] and somewhat lower than the distances with $HDABCO^+$ ions already reported [mean value 2.97(2) Å]. However, the hydrogen bonds in the last case were bifurcated ones. The location of those cations with respect to the aromatic rings deserve some comments. Each triphenol molecule defines two concave shallow cavities with its ring pairs 1–2 and 2–3; the first one corresponds to two complexed phenolic units, the second to one complexed and one uncomplexed unit. The concave faces of these cavities are directed in opposite directions. As illustrated in Fig. 6, each $HDABCO^+$ cation bonded to a uranyl ion is facing the concave side of the cavity corresponding to the phenolic units complexing the same uranyl ion (rings 1,2) and also the cavity defined by the rings 2,3 of a neighbouring molecule. Such an organization is reminiscent of the inclusion of small organic molecules in the cavity of calixarenes, with $CH_2 \cdots \pi$ interactions.

By contrast with the diphenol **1**, **2** reacts readily with uranyl ions in a basic medium. However, the bonding mode of **2** is bidentate and the third phenolic unit is not involved in the complexation. One can notice that the complex is not disrupted in $CDCl_3$ solution, as indicated by ^1H NMR results (see Experimental section), which confirm also the bonding mode, since the signals associated with the two complexed phenolic rings undergo a downfield shift and are separated from the other ones. Two out of the three phenolic units are deprotonated (as indicated both by the crystal structure and ^1H NMR results), which would prevent stabilization of the anion by hydrogen bonding in the uncomplexed form. However, the acid-enhancing effect of uranyl ions, previously invoked in the case of calixarenes,[1a,d,e,g] may stabilize this high deprotonation degree. The co-ordination of two tridentate triphenols is unlikely since the presence of six donor atoms in or near the equatorial plane of uranyl ions is only observed with small-bite bidentate ligands such as nitrate, carbonate or carboxylate ions. The crown ethers such as 18-crown-6 and its derivatives can be bonded to the uranyl ion by their six oxygen atoms[1c] but the presence of two carbon atoms between consecutive donor atoms seems to be the limit for such a bonding mode.[1i] As a confirmation of this assumption, it can be noted that, among *p-tert*-butylcalix[*n*]arenes with $n = 5–8$, the molecule with $n = 6$ is the only one which gives an 'external' complex with uranyl, with two cations bridging two face-to-face calixarene units.[1d] This is likely due to a lower rim size too large and not well organized to complex one uranyl ion and too small to include two ions. The larger size of calix[7]arene is compatible with the presence of one or two uranyl ions in its cavity, depending upon the experimental conditions and the calixarene conformation,[1f,g] while calix[8]arenes have always been observed to complex two uranyl ions in their oxygen atoms array.[1b,c] It can be concluded that the same reasons that prevent *p-tert*-butylcalix[6]arene from complexing the uranyl ion in its lower rim prevent also the triphenol **2**, analogous to half a *p-tert*-butylcalix[6]arene, from behaving as a tridentate ligand, at least with the presently observed stoichiometry.

References

1 (*a*) J. M. Harrowfield, M. I. Ogden and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1991, 979; (*b*) P. Thuéry, N. Keller, M. Lance, J. D. Vigner and M. Nierlich, *Acta Crystallogr., Sect. C*, 1995, **51**, 1570; (*c*) P. Thuéry, N. Keller, M. Lance, J. D. Vigner and M. Nierlich, *New. J. Chem.*, 1995, **19**, 619; (*d*) P. Thuéry, M. Lance and M. Nierlich, *Supramol. Chem.*, 1996, **7**, 183; (*e*) P. Thuéry and M. Nierlich, *J. Incl. Phenom.*, 1997, **27**, 13; (*f*) P. Thuéry, M. Nierlich, M. I. Ogden and J. M. Harrowfield, *Supramol. Chem.*, 1998, **9**, 297; (*g*) P. Thuéry, M. Nierlich, B. Souley, Z. Asfari and J. Vicens, *J. Chem. Soc., Dalton Trans.*, 1999, 2589; (*h*) P. Thuéry, M. Nierlich, B. Masci, Z. Asfari and J. Vicens, *J. Chem. Soc., Dalton Trans.*, 1999, 3151; (*i*) for a review, see J. Harrowfield, *Gazz. Chim. Ital.*, 1997, **127**, 663.

2 P. Thuéry and M. Nierlich, *J. Chem. Soc., Dalton Trans.*, 1997, 1481.

3 See, for example: (*a*) A. C. Sindt-Josem and M. F. Mackay, *Aust. J. Chem.*, 1981, **34**, 81; (*b*) G. Casiraghi, M. Cornia, G. Sartori, G. Casnati, V. Bocchi and G. D. Andreetti, *Makromol. Chem.*, 1982, **183**, 2611; (*c*) E. Paulus and V. Böhmer, *Makromol. Chem.*, 1984, **185**, 1921; (*d*) G. Ferguson, R. McCrindle and A. J. McAlees, *Can. J. Chem.*, 1989, **67**, 779; (*e*) S. Usui, K. Deyama, Y. Fukazawa, T. Sone and Y. Ohba, *Chem. Lett.*, 1991, 1387; (*f*) M. Perrin and D. Oehler, in *Calixarenes: a Versatile Class of Macrocyclic Compounds*, eds. J. Vicens and V. Böhmer, Kluwer, Dordrecht, 1991, pp. 68–71 and references therein.

4 See, for example: M. Mazzanti, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1989, 1793; P. J. Toscano, E. J. Schermerhorn, C. Dettelbacher, D. Macherone and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1991, 933; M. H. Chisholm, I. P. Parkin, K. Folting, E. B. Lubkovsky and W. E. Streib, *J. Chem. Soc., Chem. Commun.*, 1991, 1673; F. Corazza, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1991, **30**, 145; J. Okuda, S. Fokken, H. C. Kang and W. Massa, *Chem. Ber.*, 1995, **128**, 221.

5 Kappa-CCD Software, Nonius B.V., Delft, 1998.

6 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.

7 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

8 G. M. Sheldrick, SHELXL 93: Program for the Refinement of Crystal Structures, University of Göttingen, 1993.

9 A. L. Spek, PLATON, University of Utrecht, 1998.

10 G. M. Sheldrick, SHELXTL, Version 5.1, University of Göttingen (distributed by Bruker AXS, Madison, WI), 1999.

11 F. Ugozzoli and G. D. Andreetti, *J. Inclusion Phenom.*, 1992, **13**, 337.

12 C. Schmidt, M. Kumar, W. Vogt and V. Böhmer, *Tetrahedron*, 1999, **55**, 7819.