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Versatility of large homooxacalixarenes as ligands in polymetallic complexes: the case of UO_2^{2+} and *p-tert*-butyloctahomotetraoxacalix[8]arene

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Abstract

The coordination of uranyl ions in their complexes with *p-tert*-butyloctahomotetraoxacalix[8]arene (LH_8) is shown to be strongly dependent on the synthesis conditions. The tetranuclear complex $[(UO_2)_4O_4(LH_8)] \cdot 10CH_3OH$ (**1**) differs from the previously reported, octa-phenoxide one by the coordination of all the ether groups and the subsequent rotation of the tetra-uranate cluster with respect to the macrocycle. In the presence of pyridine, the complex $[(UO_2)_2(py)_4(LH_4)] \cdot py$ (**2**) is formed, in which the partially deprotonated ligand is bound to two independent uranyl species by four phenoxide and two ether groups only, thus evidencing the decrease in nuclearity due to a coordinating base (pyridine) preventing cluster formation through bridging ions.

Keywords: Uranyl ion; Calixarenes; Homooxacalixarenes; Clusters; Crystal structures

1. Introduction

Calix[*n*]arenes and homooxacalix[*n*]arenes larger than the most usual ones ($n = 4$ or 6 for calixarenes, 3 or 4 for homooxacalixarenes), with their array of phenol/phenoxide groups, are particularly well suited to build polynuclear metallic complexes, with a marked propensity to encompass metal ion clusters [1,2] and the recent breakthrough towards very large macrocycles [3–5] should further benefit this approach. *p-R*-calix[8]arene and its derivatives, which have been known for long, were used early to get polynuclear complexes, for example hexa-aluminium(III) [6] or bis-titanium(IV) [7] complexes. More recently, tri- and tetra-tungsten(VI) complexes with this macrocycle were reported [8], as well as oligonuclear europium(III) complexes with calix[8]arene, *p-tert*-butylcalix[7]arene and *p-tert*-butylcalix[9]arene, which illustrate the possibility to complex metal ion clusters of various sizes, up to heptanuclear [9]. A large number of polynuclear complexes with these and other, smaller or larger, calixarenes and homooxacalixarenes, are known in the case of the uranyl ion UO_2^{2+}, which makes this family of complexes the most extended in terms of calixarene size [1,2,10–12]. *p-tert*-Butyloctahomotetraoxacalix[8]arene (LH_8) (Scheme 1), gives one of the largest species in this family, with four uranyl ions in the cavity of the octa-anionic ligand, bound to phenoxide groups and bridged by hydroxide and water moieties [10]. In the presence of rubidium hydroxide as a base, the same macrocycle has recently been reported to form a mixed uranyl/rubidium complex of much different geometry, in which two uranyl ions are complexed in 'external' fashion and bridge two macrocycles [13]. Up to now, the number of uranyl ions complexed in the calixarene/homooxacalixarene cavity has been shown to be well correlated to the macrocycle size [10]. We report herein the crystal structure of two new uranyl complexes with LH_8, which show some new features with respect to this general trend and evidence the versatility of the large

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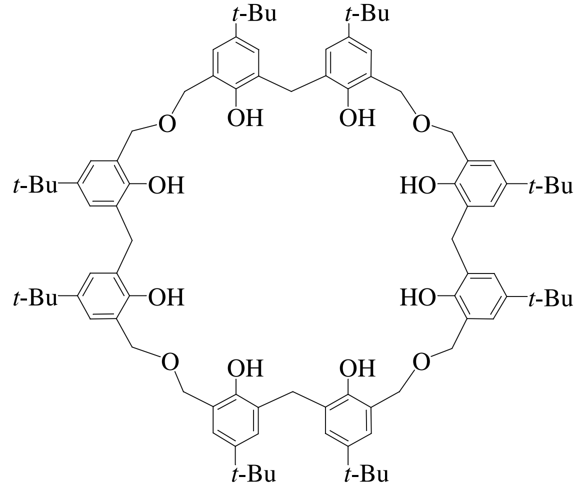


Scheme 1. *p-tert*-Butyloctahomotetraoxacalix[8]arene LH_8.

and highly flexible homooxacalixarenes as polynucleating ligands.

2. Experimental

2.1. Synthesis

The ligand *p-tert*-butyloctahomotetraoxacalix[8]arene LH_8 was synthesized as previously reported [4].

2.1.1. $[(UO_2)_4O_4(LH_8)]\cdot 10CH_3OH$ (1)

LH_8 (10 mg, 0.0074 mmol) was dissolved in $CHCl_3/CH_3OH$ 1:1 (20 ml) in the presence of NaOH (2.5 mg, 0.063 mmol). $UO_2(NO_3)_2\cdot 6H_2O$ (18 mg, 0.036 mmol) in methanol (10 ml) was added dropwise, resulting in an orange solution which was stirred at room temperature for 15 min. Unreacted NaOH crystallized and was filtered off. Dark orange single crystals, mixed with an orange powder, were obtained on slow evaporation after several recrystallizations in $CHCl_3/CH_3OH$ 1:1. Contrary to what was expected and as shown by the crystal structure determination, no deprotonation of the homooxacalixarene, even partial, occurred in this case (or at least is present in the final product), whereas it is a common trend with the various basic media currently used (in particular primary, secondary or tertiary amines).

2.1.2. $[(UO_2)_2(py)_4(LH_4)]\cdot py$ (2)

LH_8 (23 mg, 0.017 mmol) was dissolved in $CHCl_3/CH_3OH$ 1:1 (50 ml). $UO_2(NO_3)_2\cdot 6H_2O$ (37 mg, 0.074 mmol) in pyridine (10 ml) was added dropwise, resulting in an orange solution which was refluxed for 15 min. Dark orange single crystals of very low quality, mixed with an orange powder, were obtained on slow evaporation.

2.2. Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer [14] using graphite-monochromated Mo Kα radiation (λ 0.71073 Å). The crystals were introduced in glass capillaries with a protecting 'Paratone-N' oil (Hampton Research) 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 [15]. The structures were solved by direct methods (**1**) or Patterson map interpretation (**2**) with SHELXS 97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL 97 [16]. Absorption effects were corrected empirically with the program DELABS from PLATON [17]. All non-hydrogen atoms were refined with anisotropic displacement parameters. In compound **1**, one solvent molecule is disordered over two symmetry-related positions and has been affected with a 0.5 occupancy factor. In compound **2**, the pyridine solvent molecule has been refined as an idealized hexagon and has been affected with a 0.5 occupancy factor so as to keep an acceptable displacement parameter. Some restraints on bond lengths and/or displacement parameters were applied for the terminal carbon atoms of the *tert*-butyl group and the atoms of the badly resolved solvent molecules in **1**. Soft restraints on displacement parameters have been applied to the carbon atoms in compound **2**, to avoid divergence of the anisotropic refinement. The hydrogen atoms bound to oxygen atoms were not found, nor introduced. All the other hydrogen atoms were introduced at calculated positions and were treated 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. In spite of its rather low quality, the crystal structure of compound **2** gives unambiguously the main features of the complex, which are of interest for the present discussion. Crystal data and structure refinement parameters are given in Table 1 and selected bond lengths and angles in Table 2. The molecular plots were drawn with SHELXTL [18]. All calculations were performed on a Silicon Graphics workstation.

3. Discussion

The tetranuclear complex $[(UO_2)_4O_4(LH_8)]\cdot 10CH_3OH$ (**1**) is represented in Fig. 1. This compound is highly symmetric, in any case more than most other uranyl complexes of large calixarenes/homooxacalixarenes, since it crystallizes in the tetragonal space group $I\bar{4}2m$, with only one uranium atom and one phenolic group included in the asymmetric unit. By contrast, the

Table 1
Crystal data and structure refinement details

	1	**2**
Empirical formula	$C_{102}H_{160}O_{34}U_4$	$C_{117}H_{141}N_5O_{16}U_2$
M (g mol^{-1})	2882.42	2349.41
Crystal system	tetragonal	triclinic
Space group	$I\,42\,m$	$P\bar{1}$
a (Å)	18.1062(9)	14.161(3)
b (Å)	18.1062(9)	14.733(3)
c (Å)	17.3045(10)	15.450(3)
α (°)	90	89.113(16)
β (°)	90	74.243(7)
γ (°)	90	66.414(12)
V (Å^3)	5673.0(5)	2827.2(10)
Z	2	1
D_{calc} (g cm^{-3})	1.687	1.380
μ (mm^{-1})	5.767	2.923
Crystal size (mm)	$0.22 \times 0.20 \times 0.05$	$0.10 \times 0.10 \times 0.03$
F(000)	2824	1190
θ Range (°)	2.8–25.7	5.1–25.7
T (K)	100(2)	100(2)
Number of data collected	19,451	13,304
Number of unique data	2824	8582
Number of 'observed' data [$I > 2\sigma(I)$]	2232	2015
R_{int}	0.063	0.113
Number of parameters	185	683
R_1[a]	0.050	0.117
wR_2[b]	0.130	0.188
S	1.028	0.925
$\Delta\rho_{min}$ (e Å^{-3})	−1.09	−0.46
$\Delta\rho_{max}$ (e Å^{-3})	1.31	0.46

[a] $R_1 = \sum ||F_o| - |F_c|| / |F_o|$ ("observed" reflections).
[b] $wR_2 = [\sum w(|F_o^2| - |F_c^2|)^2 / \sum w|F_o^2|^2]^{1/2}$ ("observed" reflections).

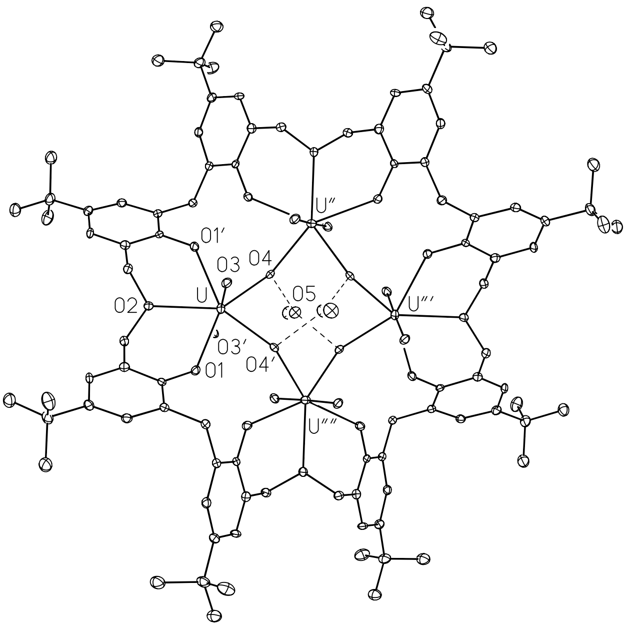


Fig. 1. View of the complex $[(UO_2)_4O_4(LH_8)] \cdot 10CH_3OH$ (**1**). Hydrogen atoms and solvent molecules (except for the hydrogen bonded ones) have been omitted for clarity. Possible hydrogen bonds are represented as dashed lines. Displacement ellipsoids are drawn at the 10% probability level. Symmetry codes: ′, $-x, y, -z$; ″, $y-1, 1-x, -z$; ‴, $-x, 2-y, z$; ⁗, $1-y, 1+x, -z$.

complex previously reported with the same ligand, $[HNEt_3]_2[(UO_2)_4L(OH)_2(H_2O)_4] \cdot 1.5NEt_3 \cdot 2.5H_2O \cdot CH_3OH$ (**3**) crystallizes with two independent, but nearly identical, molecules in the asymmetric unit [10]. Complex **1** possesses a crystallographic S_4 axis perpendicular to its mean plane and parallel to the c axis, two C_2 axis perpendicular to the former and containing the uranium and ether oxygen atoms and two σ_d symmetry planes containing the diametrically located methylene links, which results in a D_{2d} point symmetry. Even if compounds **1** and **3** share many common features, both comprising four uranyl ions in the macrocycle cavity, with all phenol/phenoxide groups coordinated, they present nevertheless some important differences. In complex **3**, each uranyl ion is bound, in its equatorial plane, to two phenoxide groups pertaining to aromatic rings separated by a methylene link, and to two water and one hydroxide moieties ensuring equatorial five-coordination and bridging with the two neighbouring

Table 2
Environment of the uranium atoms in compounds **1** and **2**: selected distances (Å) and angles (°)

Compound	Bond distances (Å)		Bond angles (°)	
1	U–O1	2.448(7)	O1–U–O2	68.91(17)
	U–O2	2.457(9)	O1–U–O4′	71.7(3)
	U–O3	1.799(7)	O4–U–O4′	79.5(5)
	U–O4	2.300(4)	O3–U–O3′	178.4(5)
	U···U″	4.2798(6)		
2	U–O1	2.164(17)	O1–U–O2	69.8(7)
	U–O2	2.62(2)	O2–U–O3	68.1(7)
	U–O3	2.223(15)	O1–U–N1	77.0(7)
	U–N1	2.58(2)	O3–U–N2	74.2(6)
	U–N2	2.51(2)	N1–U–N2	72.4(6)
	U–O7	1.792(14)	O7–U–O8	171.1(9)
	U–O8	1.700(16)		

Symmetry codes: ′, $-x, y, -z$; ″, $y-1, 1-x, -z$.

cations. In complex **1**, each uranyl ion is bound to two phenolic groups pertaining to aromatic rings separated by an ether-containing link and also to the ether oxygen atom of this link, and to two bridging O^{2-} ions, which results also in a pentagonal bipyramidal environment for the uranium atom. The U–O1 bond length in **1**, 2.448(7) Å, is much larger than the distances generally observed for uranyl–phenoxide bonds which, in similar complexes, are in the range 2.20–2.30 Å, and it is close to the bond lengths measured in the binuclear uranyl complexes of *p*-*tert*-butylcalix[8]arene for uranyl–phenol bonds, which are in the range 2.45(2)–2.619(9) [mean value 2.53(7)] Å [19]. Furthermore, the U–O4 bond length, 2.300(4) Å, is located in the lower part of the range of usual values for uranyl bonding to hydroxo groups in comparable complexes, 2.287(14)–2.39(2) [mean value 2.34(3)] Å [11,19] whereas it is slightly larger than the values for uranyl bonding to oxo ions, 2.12(2)–2.28(2) [mean value 2.21(6)] Å [20]. These comparisons permit to make with some confidence the hypothesis that the phenol groups in **1** are not deprotonated and that the bridging species are μ_2-oxo ions. However, as often in calixarene/homooxacalixarene complexes involving extra water, hydroxo or oxo ligands, the precise location of protons and charges may be somewhat questionable. It may not be completely ruled out that the bridging species be μ_2-hydroxo ligands and four phenolic groups be deprotonated, giving the formula $[(UO_2)_4(OH)_4(LH_4)] \cdot 10CH_3OH$. However, the assignment of charges proposed above seems to be in better agreement with the geometric parameters. The U–O2 bond length, 2.457(9) Å, is smaller than the U–O(ether) bond lengths in other homooxacalixarene complexes, which are in the range 2.609(8)–2.950(4) Å, which may result from the lesser donor ability of phenol with respect to the usual phenoxide groups. This U–O(ether) distance is also slightly smaller than those in uranyl complexes of 18-crown-6 (2.50–2.58 Å) [19b], but it is comparable to the mean value of 2.43(5) Å for U–O(thf) bond lengths reported in the Cambridge Structural Database [21]. The five donor atoms in **1** define a plane with a maximum deviation of 0.156(9) Å for the bridging atoms and the uranium atom is located in this mean plane, as well as the ether atom O2. The mean O_5 planes relative to adjacent uranyl ions make dihedral angles of 34.9(2)°.

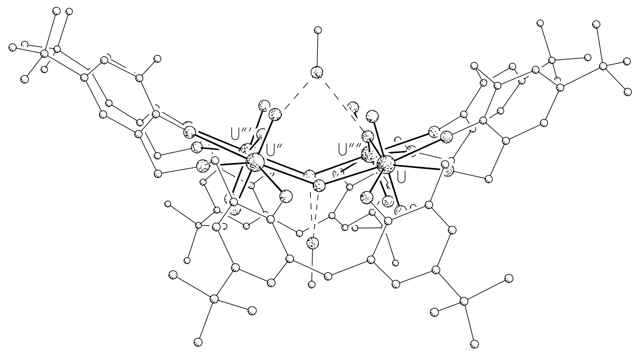
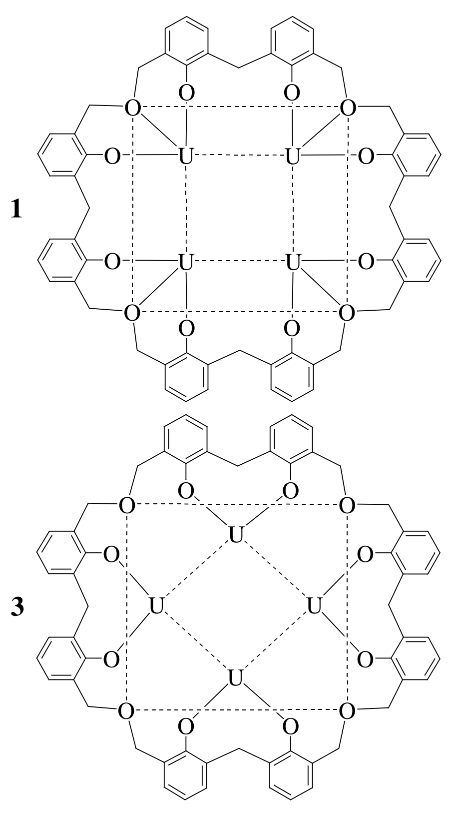


Fig. 2. View of the complex $[(UO_2)_4O_4(LH_8)] \cdot 10CH_3OH$ (**1**). Hydrogen atoms and solvent molecules (except for the hydrogen bonded ones) have been omitted for clarity. Possible hydrogen bonds are represented as dashed lines. The carbon atoms have been arbitrarily reduced for clarity. Symmetry codes: ″, $y-1, 1-x, -z$; ‴, $-x, 2-y, z$; ⁗, $1-y, 1+x, -z$.

The macrocycle conformation in complexes **1** and **3** varies according to the different coordination modes. In both cases, as shown in Fig. 2 for **1**, the ligand adopts a saddle shape, but the fine details differ. In the notation of Kanamathareddy and Gutsche [22], the conformation of *p*-*tert*-butylcalix[8]arene in its binuclear uranyl complex can be described as (uudduudd). If the ether bridges are introduced in this notation as (b), the conformation in **3** is [ud(b)du(b)ud(b)du(b)] whereas that in **1** is [uu(b)dd(b)uu(b)dd(b)], i.e., closer to that of *p*-*tert*-butylcalix[8]arene, with ether groups located between 'up' and 'down' aromatic rings (and also between 'up' and 'down' parts of the saddle). This conformation in **1** brings the four ether oxygen atoms close to the mean plane of the molecule, in a position suitable for uranium complexation. The two torsion angles defined by the ether bridges in **1** are equal to 100.0°, which is an unusual value bringing O2 closer to the uranium atom, as evidenced in Fig. 1. A comparable situation has been observed in the mixed uranyl/rubidium complex with the same macrocycle, with torsion angles of 73° and 80° for an ether group directed towards the cavity centre [13]. An easy way of visualising the difference between **1** and **3** is to consider the parallelogram (square in **1**) built by the four uranium atoms and the other one (also a square in **1**) corresponding to the four ether oxygen atoms (Scheme 2). These two parallelograms have parallel sides in **1**, with bonds between their respective corners, whereas they are rotated by about 45° one with respect to the other in **3**. Both compounds comprise a tetra-uranate cluster, albeit with different bridges (simple and double bridges coexist in **3**), but oriented and bound differently. The square shape of the cluster in **1**, with a side length of 4.2798(6) Å, matches the circular shape of the macrocycle [with a distance of 7.754(12) Å between successive ether oxygen atoms], whereas the slightly elongated parallelogram shape of the cluster in **3**, with mean side lengths of 4.96(10) and 4.08(3) Å is fit to the macrocycle elongated shape [with mean distances of 13.4(1) and 12.0(2) Å between diametrically located ether oxygen atoms]. The dihedral angle between the aromatic ring and the mean plane defined by the four uranium and four ether oxygen atoms in **1** is 54.7(3)° and the dihedral angle between two aromatic rings separated by a methylene bridge is 68.2(4)°.



Scheme 2. Schematic representation of the different bonding geometries of the tetrauranate cluster in complexes **1** and **3**. Uranyl oxo atoms, oxygen bridges, *tert*-butyl groups and hydrogen atoms are omitted. The parallelograms discussed in the text are shown in dashed lines.

Complex **1** crystallizes with ten methanol molecules, among which eight are simply entrapped in the lattice whereas the two other ones, corresponding to O5 and its symmetry equivalent, are located on the S_4 main axis and are involved in possible hydrogen bonds with the two proximal oxo bridges, as shown in Figs. 1 and 2 [O5···O4 distance 2.77(2) Å].

The complex $[(UO_2)_2(py)_4(LH_4)]\cdot py$ (**2**) provides a very different arrangement, as evidenced in Fig. 3. This compound crystallizes in the triclinic space group $P\bar{1}$, with half a complex molecule in the asymmetric unit. The complex thus belongs to the point group C_i. Two uranyl ions only are included in the macrocycle cavity, each of them bound to two phenoxide groups and the ether oxygen atom located in between, as in complex **1**, but in this case, the uranium coordination sphere is completed by two pyridine molecules, which results in the usual pentagonal bipyramidal environment. The five donor atoms define a plane with a maximum deviation of 0.23(1) Å, the uranium atom being at 0.033(9) Å from this plane. The mean U–O(phenoxide), U–O(ether) and U–N bond lengths are 2.19(3), 2.62(2) and 2.55(4) Å, respectively, in good agreement with usual values. By contrast with all the previous cases of uranyl 'internal' complexation with large calixarenes/homooxacalixarenes, the two cations in **2** are isolated one from the other, with a U···U distance of 8.161(3) Å, thus leaving an empty space at the centre of the macrocycle.

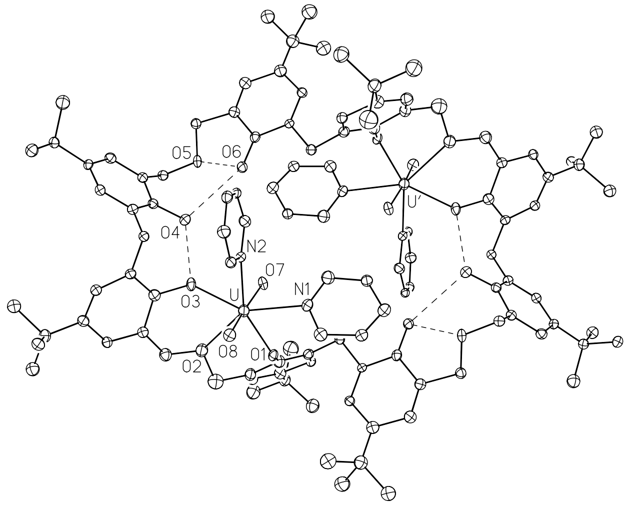


Fig. 3. View of the complex $[(UO_2)_2(py)_4(LH_4)]\cdot py$ (**2**). The hydrogen atoms and the solvent molecule have been omitted for clarity. Possible hydrogen bonds are represented as dashed lines. Displacement ellipsoids are drawn at the 10% probability level. Symmetry code: ′, $-x, 1-y, 1-z$.

The conformation of the homooxacalixarene in **2** is far from being as regular as those in **1** and **3** and a proper reference plane cannot be found for the whole molecule, but the five donor atoms O1, O2, O3, N1 and N2 can be taken to define a reference plane for each half-molecule (Fig. 4). In the notation used above and beginning by the phenolic ring associated to O1, the conformation for the half-molecule can be given as

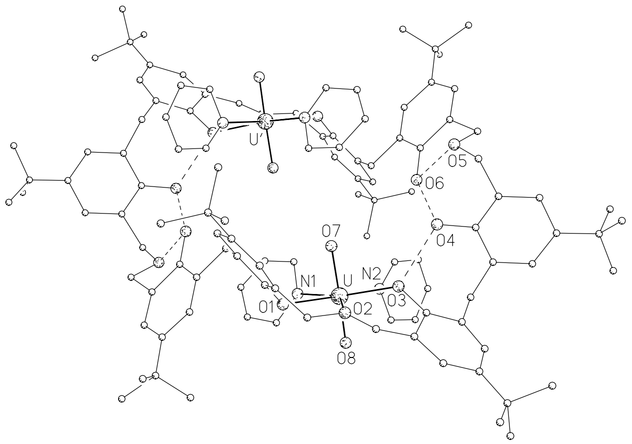


Fig. 4. View of the complex $[(UO_2)_2(py)_4(LH_4)]\cdot py$ (**2**) approximately parallel to the uranyl ions coordination planes. The hydrogen atoms and the solvent molecule have been omitted for clarity. Possible hydrogen bonds are represented as dashed lines. The carbon atoms have been arbitrarily reduced for clarity. Symmetry code: ′, $-x, 1-y, 1-z$.

[d(b)uu(b)d]. The dihedral angles between the four aromatic rings and the mean plane are 54.2(8)°, 43.4(7)°, 81.4(7)° and 56.0(6)°. However, the portion comprising the last two aromatic rings is buckled away towards the second half of the molecule. The distance between the two mean O_3N_2 planes is 6.4 Å. The phenolic hydrogen atoms have not been located in this structure, but the O···O distances involving the phenolic oxygen atoms O4 and O6, the ether O5 and the phenoxide O3 suggest the existence of two hydrogen bonds, a bifurcated one with O6 as donor and O4 or O5 as receptors [O6···O4 2.94(3), O6···O5 2.72(2) Å] and a second, strong one between O4 and O3 [O4···O3 2.61(3) Å]. The four phenolic rings and two ether bridges comprising the half-molecule of the repeat unit and including the oxygen atoms O1–O6 are thus held together either by coordination to one uranyl ion or by hydrogen bonding. The two half-molecules, attached by two methylene bridges, are not further connected through coordination bonds or other feeble interactions.

4. Conclusion

The question arises of the origins of the differences observed between compounds **1**, **2** and **3**. Complex **3** has been obtained, as many other uranyl/calixarene complexes, in the presence of triethylamine and synthesized and recrystallized in non-coordinating or rather poorly uranyl-coordinating solvents ($CHCl_3$, CH_3OH, CH_3CN). Octa-deprotonation and octaphenoxide complexation with no ether coordination result from that, which is expected in view of all that is known about homooxacalixarene complexation [2,10–12]. The apparent absence of deprotonation in complex **1**, and the resulting replacement of ionic uranyl–phenoxide bonds by uranyl–phenol dative ones, may be viewed as the reason why all four ether groups are also coordinated. This in turn necessitates a different location of the cations in the macrocycle cavity. Complex **2** was obtained in the presence of pyridine, which is a strongly coordinating ligand. This solvent has been often used as a recrystallization solvent in our previous work, with seemingly little effect on the complex nature and, in particular, no displacement of ligands. However, in the present case, it appears that pyridine, by completing the uranyl coordination sphere, has prevented bonding to bridging water, hydroxo or oxo species and the subsequent formation of a poly-uranate cluster, leaving four phenolic oxygen atoms uncomplexed.

We have previously shown that the prediction of the complex nuclearity from the macrocycle size must be balanced by the more or less convenient location of the ether groups among positional isomers of homooxacalixarenes [12]. The present results add some new features in the case of a large homooxacalixarene, which put also in evidence the different roles of the two coordinating sites, phenol/phenoxide and ether. It appears that the same nuclearity can be obtained with two different coordination modes, as in **1** and **3**, depending on the coordination of the ether groups, thanks to the flexibility of the molecule which changes its conformation accordingly. Comparison of complexes **1** and **3** with complex **2** shows the effect of a coordinating and nonbridging base, which reduces the nuclearity by isolating the uranyl moieties and preventing the formation of a poly-uranate cluster.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 216011 and 216012. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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