

Complexes of uranium(IV) with acyclic polyphenoxides resulting from cleavage of homooxalixarenes

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Reaction of UCl_4 with homooxalixarenes in pyridine results in cleavage of the ether bridges upon nucleophilic attack by pyridine, likely assisted by the U(IV) ion. The zwitterionic diphenoxide species bis[5-*tert*-butyl-2-oxido-3-(1-pyridiniummethyl)-phenyl]methane L^1 formed from *p*-*tert*-butyltetrahomodioxalix[4]arene, *p*-*tert*-butylhexahomotrioxalix[6]arene or *p*-*tert*-butyloctahomotetraoxalix[8]arene and the zwitterionic triphenoxide species 4-*tert*-butyl-2,6-bis[5-*tert*-butyl-2-oxido-3-(1-pyridiniummethyl)-benzyl]phenolate (L^2)⁻ formed from *p*-*tert*-butyltetrahomodioxalix[6]arene give polyphenoxide complexes of U(IV). Coordination of L^1 to UCl_4 yields the neutral complex $[\text{UCl}_4(\text{L}^1)]$ and, on further heating, the cationic $[\text{UCl}_2(\text{L}^1)_2]^{2+}$ species, whereas (L^2)⁻ gives only the neutral compound $[\text{UCl}_3(\text{L}^2)]$. In these three complexes, the metal atom is in slightly distorted octahedral environments, with bonding to all phenoxide groups. These are the first instances of U(IV) complexes with polyphenoxide ligands, resulting from unprecedented homooxalixarene cleavage.

Introduction

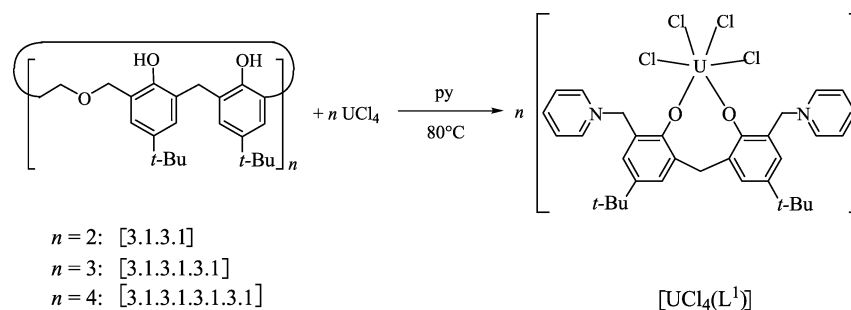
Homooxalixarenes are macrocycles closely related to calixarenes, from which they differ by one or more methylene links being replaced with 2-oxa-1,3-propylene links.¹ Owing to an extensive synthetic work, a wide range of homooxalixarenes of varying sizes (from the smallest hexahomotrioxalix[3]arene to the largest ones, equivalent in size to calix[12]arene) is now available^{1,2} and represents a new family of ligands for the coordination chemist. Recently, we have investigated the complexing properties of these molecules towards the uranyl ion, which has previously been the subject of analogous studies with calixarenes, with a particular emphasis on the molecular and supramolecular structures of the resulting complexes.³ A natural extension of this work consisted of replacing the uranyl ion by uranium ions in other, lower oxidation states: new coordination geometries and/or stoichiometries being expected from the different geometric and electronic preferences of these ions. Apart from the uranyl ion, few examples have been reported of calixarene complexes of actinides, these being limited to the Th(IV) complex of *p*-*tert*-butylcalix[8]arene⁴ and some U(V) and U(VI) complexes of *p*-*tert*-butylcalix[4,5,6]arenes.⁵ It is only very recently that the first U(IV) complex of *O*-dimethylated *p*-*tert*-butylcalix[4]arene has been reported.⁶ We decided in consequence to investigate the synthesis and crystal structure of U(IV) complexes of homooxalixarenes, but the experimental conditions used resulted in an unexpected cleavage of the ether functions and the formation of acyclic polyphenoxide uranium(IV) derivatives. Uranyl

complexes of polyphenols with two,⁷ three^{7,8} or six⁹ phenolic units have been described, but the present complexes are the first di- and tri-phenoxide complexes of U(IV). To the best of our knowledge, this is also the first report of homooxalixarene cleavage.

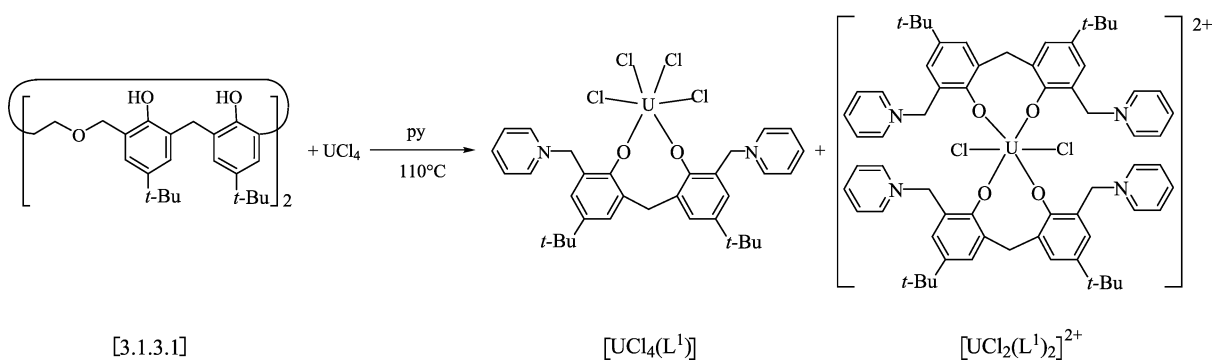
Results and discussion

Synthesis of the complexes

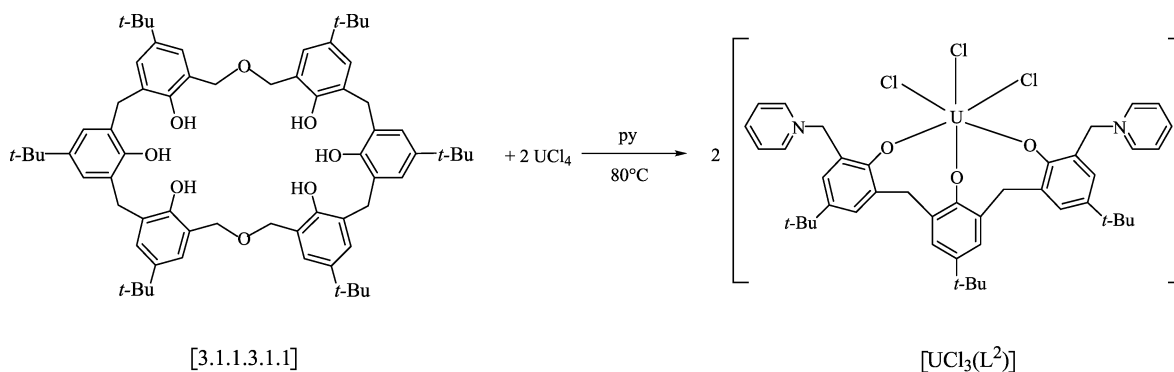
First attempts to prepare new complexes from UCl_4 and homooxalixarenes were carried out in tetrahydrofuran. In this solvent, a slow reaction occurred at 20 °C, as shown by the emergence of paramagnetically shifted signals in the ¹H NMR spectrum. However, no product could be characterized and no crystals suitable for crystallographic studies were formed. Changing tetrahydrofuran for pyridine readily gave a light green solution which, after 24 h at 80 °C, deposited bright yellow crystals. These were quite insoluble in organic solvents and could not be characterized by NMR spectroscopy; their structure was revealed by X-ray diffraction analysis. Surprisingly, as represented in Scheme 1, the same compound $[\text{UCl}_4(\text{L}^1)] \cdot 2\text{py}$ (**1**) { $\text{L}^1 = \text{bis}[5\text{-}i\text{-tert-butyl-2-oxido-3-(1-pyridiniummethyl)-phenyl]methane}$ } was obtained from the three homooxalixarenes *p*-*tert*-butyltetrahomodioxalix[4]arene (denoted [3.1.3.1] hereafter),¹⁰ *p*-*tert*-butylhexahomotrioxalix[6]arene ([3.1.3.1.3.1]) and *p*-*tert*-butyloctahomotetraoxalix[8]arene ([3.1.3.1.3.1.3.1]) which are built from the same repeated [3.1] unit. Prolonged heating at 110 °C for 3 days of a 1 : 1 mixture of



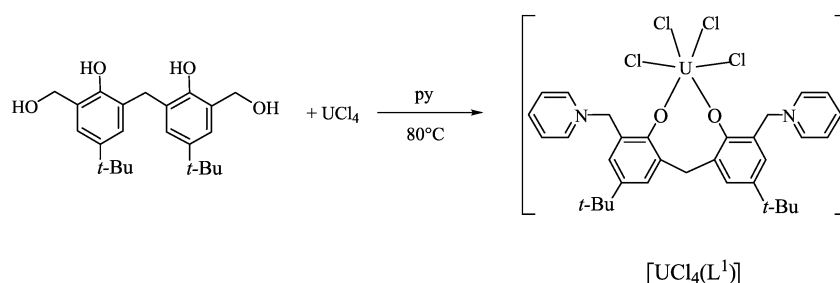
Scheme 1



Scheme 2



Scheme 3



Scheme 4

[3.1.3.1] and UCl₄ in pyridine gave yellow crystals of **1** with a small quantity of orange crystals. X-ray diffraction showed the latter to correspond to the cationic complex [UCl₂(L¹)₂]Cl₂·5py (**2**), resulting from replacement of two chloride ligands of **1** with L¹ (Scheme 2). Similar reaction of *p*-*tert*-butyltetrahydrodioxacalix[6]arene, [3.1.1.3.1.1] with UCl₄ (Scheme 3) afforded yellow needles of [UCl₃(L²)]₂py (3) which were, here again, characterized by their X-ray crystal structure { (L²)⁻ = 4-*tert*-butyl-2,6-bis[5-*tert*-butyl-2-oxido-3-(1-pyridinylmethyl)benzyl]phenolate}. Complexes **1–3** obviously result from the cleavage of the ether bridges of the homooxacalixarenes, after nucleophilic attack of pyridine onto the benzylic carbon atoms. This reaction is certainly assisted by the initial coordination of the ether oxygen atom to the uranium(IV) centre. Such cleavage reactions of benzylic ethers, which are frequently used for deprotecting hydroxyl groups, are well documented.¹¹ Lewis acids play a major role in the activation of the C–O bond rupture, as shown for example by the cleavage of the crown ether Grignard reagent 2-(bromomagnesium)-1,3-xylyl-15-crown-4 which does not take place at the benzylic oxygens likely because these are not strongly bound to the magnesium atom.¹²

The acyclic polyphenoxides L¹ and (L²)⁻ can be considered as doubly zwitterionic and are thus of a double betaine type. The easy formation of these ligands from four distinct homooxacalixarenes and the high yields of **1** and **3** highlight the remarkable efficiency of the cleavage reaction. Notably, all the ether C–O bonds of the homooxacalixarenes could be readily

broken; thus, reaction of [3.1.3.1.3.1.3.1] with 4 equivalents of UCl₄ afforded **1** with a 85% yield. Considering that the cleavage of the ether bridges of the homooxacalixarene first liberates an *ortho*-oxido benzylic alcohol, this latter should be further transformed into L¹ or (L²)⁻ upon nucleophilic attack by pyridine and elimination of a water molecule. Indeed, reaction of bis(5-*tert*-butyl-2-hydroxy-3-hydroxymethylphenyl)methane with 1 equiv. of UCl₄ in pyridine gave **1** in 87% yield (Scheme 4).

The benzylic ether functions of homooxacalixarenes are expected to be labile in acidic conditions and some ring transformation and decomposition have been reported to occur at high temperature or in strongly basic media,^{2b,13} but there is no report for a cleavage such as the presently reported one. By contrast with calixarenes, which are much stable compounds, homooxacalixarenes can be cleaved in the presence of metallic salts, which is a result to take into account if these molecules are to be used as extraction and separation agents. (It has been previously reported that the OMe bonds of hexamethoxycalix[6]arene could be cleaved upon treatment with TiCl₄ to give a macrocycle to which two bimetallic Cl₃TiOTiCl₂ fragments are attached.¹⁴)

Crystal structures of the complexes

The asymmetric unit in **1** contains one complex and two pyridine molecules. The former presents a pseudo-symmetry plane containing U, Cl3, Cl4 and the methylenic carbon bridge of L¹.

Table 1 Environment of the uranium atom in compounds **1–3**: selected distances (Å) and angles (°)^a

	1		2		3
U–O1	2.138(4)	U–O1	2.194(8)	U–O1	2.148(9)
U–O2	2.168(4)	U–O2	2.157(8)	U–O2	2.168(6)
U–Cl1	2.6682(15)	U–Cl1	2.724(4)	U–O3	2.208(6)
U–Cl2	2.6692(16)	O1–U–O2	83.5(3)	U–Cl1	2.713(3)
U–Cl3	2.6636(15)	O1–U–O1'	95.6(4)	U–Cl2	2.719(3)
U–Cl4	2.6708(15)	O1–U–O2'	93.2(3)	U–Cl3	2.686(4)
O1–U–O2	88.82(16)	O2–U–O2'	175.1(4)	O1–U–O2	88.9(3)
		Cl1–U–Cl1'	90.38(15)	O2–U–O3	87.7(2)
				O1–U–O3	97.9(3)

^a Symmetry code: ' = -x, y, 1.5 - z.

The uranium atom is bound to the two phenoxide oxygen atoms and to four chlorine atoms, in a slightly distorted octahedral environment, with the two oxygen atoms in *cis* positions (Fig. 1). The U–O bond lengths have a mean value of 2.15(2) Å (Table 1), which is in the range of U(IV)–O bond lengths for terminally coordinated phenoxide groups^{15–17} which vary from 2.073(9) Å in [U(OAr)₂I₂(THF)]¹⁵ (Ar = 2,6-Bu^t₂C₆H₃) to 2.188(8) Å in [U(NN₃)(OPh)OBu^tLi(THF)]¹⁶ [NN₃ = N(CH₂-CH₂NSiMe₃)₃]. In contrast with the variation in ionic radii of U⁴⁺ and UO₂²⁺,¹⁸ the U–O distances in **1** are shorter by about 0.09 Å than the U–O(phenoxide) distances in uranyl complexes with di- [mean value 2.25(2) Å], tri- [2.23(5) Å] and hexaphenoxide ligands [2.21(5) Å] [global mean value 2.24(4) Å].^{7–9} The mean values of the U–O(phenoxide) bond lengths determined in calixarene complexes are 2.09(2) Å for the unique other U(IV) complex,⁶ 2.13(8) Å for a U(V,VI) mixed valence complex, 2.15(3) Å for U(V) and 2.13(2) Å for U(VI),⁵ *i.e.* either shorter than those in **1** in the first case or identical in the others, notwithstanding the variations in oxidation states. The U–Cl bond lengths have a mean value of 2.668(3) Å, close to the mean value of 2.61(6) Å calculated from the data in the Cambridge Structural Database¹⁹ (non-bridging chlorines only). The angles defined by adjacent donor atoms around uranium are in the range 85.87(12)–93.39(5)°, showing little distortion of the octahedron. The diphenoxide ligand adopts a “butterfly” conformation, with a dihedral angle of 76.3(2)° between the two aromatic rings, analogous to that in the 1 : 2 uranyl complex of a related diphenol with hydroxymethyl terminal groups [71.4(6)–79.6(7)°].⁷ The crystal packing brings molecules related by the symmetry centre in such a position that the pyridinium rings are involved in intermolecular π – π stacking interactions (Fig. 2), with a distance between the centroids of 3.72 Å, an interplanar spacing of 3.65 Å, a centroid offset of 0.71 Å and a shortest C \cdots C contact of 3.569 Å. The packing in uranyl complexes of calixarenes, homooxalixarenes and acyclic

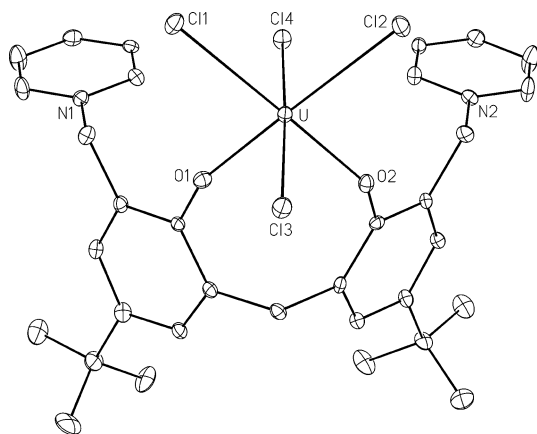


Fig. 1 View of the complex [UCl₄(L¹)]·2py, **1**. The solvent molecules and hydrogen atoms are omitted for clarity. The displacement ellipsoids are drawn at the 20% probability level.

polyphenols is largely determined by extensive hydrogen bonding interactions, some of those involving the uranyl oxo groups.^{3,7–9} In the present case, such interactions are absent and, apart from van der Waals interactions, π – π stacking interactions seem to be dominant, which is certainly largely facilitated by the orientational flexibility of the pyridinium rings.

Compound **2**, in which the complex itself is cationic, crystallizes with half a complex molecule, one unbound chlorine atom (disordered over two sites) and 2.5 pyridine molecules in the repeat unit. The uranium atom, which is located on a binary axis (Fig. 3), is in an octahedral environment slightly more distorted than in compound **1** [angles defined by adjacent donor atoms around uranium in the range 83.5(3)–97.4(2)°]. The O1–U–O2 angle in particular is smaller in **2** [83.5(3)°] than in **1** [88.82(16)°], which is to be ascribed to U–O bond lengths slightly longer in the former [mean value 2.18(3) Å] since the dihedral angle between the two phenolic rings [76.2(4)°] is identical to that in **1**. The O2 atom and its symmetry-related equivalent are in *trans* positions whereas the other oxygen atom is *trans* to a chlorine atom. The U–Cl bond lengths are slightly longer in **2** [2.724(4) Å] than in **1** [2.668(3) Å]. The pyridinium groups in each diphenoxide ligands are dissymmetrically located, and there is no pseudo-symmetry element as in **1**. The pyridinium arm containing N1 is directed away from the “cup” defined by the two phenoxide rings, whereas the second one, containing N2, is directed towards it. This is likely to result from packing effects since the N2-containing pyridinium rings pertaining to two neighbouring molecules (related by a symmetry centre) are facing each other with rather feeble π – π stacking interactions [distance between the centroids 3.87 Å, interplanar spacing 3.38 Å, centroid offset 1.88 Å (much larger than in **1**) and shortest C \cdots C contact 3.459 Å]. Furthermore, the N2-containing pyridinium group of each molecule is located in the “cup” of the other one, with possible CH(pyridinium ring) \cdots π (phenoxide) interactions [shortest one: H \cdots centroid distance 2.693 Å, C \cdots centroid distance 3.543 Å, C–H \cdots centroid angle 152°]. Such CH– π interactions, albeit feeble ones, are often observed and have been lately much documented.²⁰ Another significant π – π stacking interaction involves one phenoxide ring and a pyridine solvent molecule.

In compound **3**, the uranium atom is bound to the three phenoxide oxygens of (L²)[–], which is wrapped around the metal and assumes a “half-cone” shape, and to three chlorine atoms (Fig. 4). The U–O bond lengths have a mean value of 2.17(3) Å, identical to that in **2** and the U–Cl bond lengths have a mean value of 2.71(2) Å. The uranium coordination geometry is *fac*-octahedral, with the angles defined by adjacent atoms in the range 86.3(2)–97.9(3)°, the latter value corresponding to O1 and O3. The plane defined by O1, O2 and O3 can be taken as a reference to describe the geometry of the triphenoxide ligand. The dihedral angles between this plane and the three phenoxide rings are 46.7(3), 86.7(3) and 46.6(4)°, and the uranium atom is at 1.218(4) Å from it. The O \cdots O distances are O1 \cdots O2 3.02(1), O2 \cdots O3 3.03(1), which are close to their counterparts in uranyl calixarene complexes, and O1 \cdots O3 3.29(1) Å.

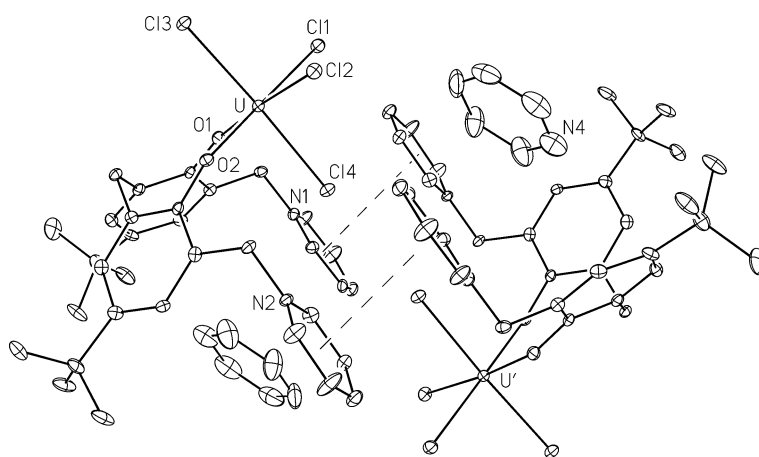


Fig. 2 View showing the π - π stacking interactions (dashed lines) in the complex $[\text{UCl}_4(\text{L}^1)]\cdot 2\text{py}$, **1**. Two pyridine solvent molecules and the hydrogen atoms are omitted for clarity. The displacement ellipsoids are drawn at the 20% probability level.

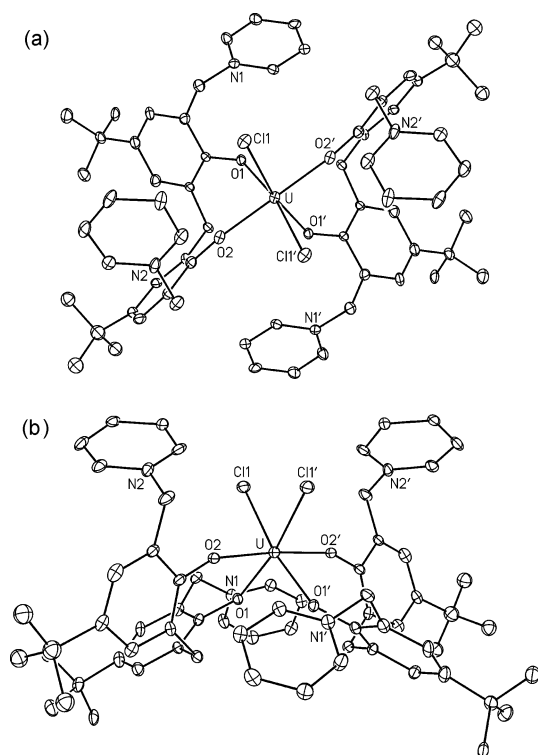


Fig. 3 Two views of the complex $[\text{UCl}_2(\text{L}^1)_2]\text{Cl}_2\cdot 5\text{py}$, **2**. The counterions, solvent molecules and hydrogen atoms are omitted for clarity. The displacement ellipsoids are drawn at the 10% probability level. Symmetry code: $' -x, y, 1.5 - z$.

These geometric parameters indicate that L^2 in **3** can be viewed as a partial calix[4]arene in a distorted “cone” conformation, with the two terminal rings closer to the reference plane than the central one. This is confirmed by the four torsion angles defined by the methylene bridges, which are all “*gauche*”, with some distortion (68.3–99.7°), and define a (+, +, +) sequence typical of a “cone” arrangement.²¹ The two pyridinium groups behave differently: the first one is directed towards the “inside” of the complex whereas the second one is directed outwards. However, there are no significant intermolecular π - π stacking interactions in the packing, apart from some involving pyridine solvent molecules. One pyridine is located in the “cup” defined by the complex, which is frequently observed with calixarene complexes as well. The present complex is of interest when compared to those obtained with the uranyl ion. Calix[4]arene is notoriously too small to accommodate a central uranyl ion with its four oxygen atoms in the equatorial plane and it complexes this ion in an external, unidentate, fashion, whereas the larger thiocalix[4]arene is able to give an internal complex with

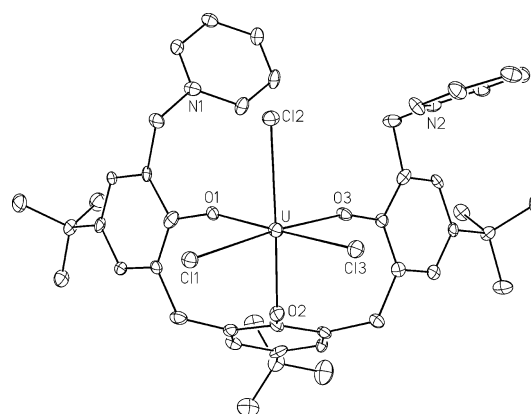


Fig. 4 View of the complex $[\text{UCl}_3(\text{L}^2)]\cdot 2\text{py}$, **3**. The solvent molecules and hydrogen atoms are omitted for clarity. The displacement ellipsoids are drawn at the 20% probability level.

tetraphenoxide equatorial coordination.²² It may be noted however that, notwithstanding the larger ionic radius of $\text{U}(\text{iv})$, *O*-dimethylated *p*-*tert*-butylcalix[4]arene (in a much distorted “cone” conformation) is able to complex this cation through its two phenoxide and two ether oxygen atoms, *i.e.* close to the lower rim cavity, the presence of bridging chlorine atoms resulting in the formation of a cyclic trimer.⁶ On the other hand, acyclic triphenols H_3L have been observed to bind to the uranyl ion by two oxygen atoms only, to give $[\text{UO}_2(\text{HL})_2]^{2-}$ species with square planar equatorial geometries, which is likely due to the impossibility to bring the three phenoxides at a convenient distance from the uranyl ion and in its equatorial plane.^{7,8} By contrast, triphenoxide complexation of $\text{U}(\text{iv})$ by $(\text{L}^2)^-$ is possible owing to the very different bonding requirements of this ion. No 1 : 2 species analogous to compound **2** has been isolated with $(\text{L}^2)^-$. Replacement of the three chlorine atoms by a second triphenoxide ligand, giving a bis(triphenoxide) octahedral environment analogous to that previously observed in a $\text{U}(\text{vi})$ complex of *p*-*tert*-butylcalix[6]arene,^{5b} seems possible on geometric grounds, but is probably hampered by the steric hindrance of the bulky pyridinium groups and/or the electrostatic repulsion that would arise between these groups in the complex.

Experimental

All preparations and experiments were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. The homooxalixarenes,^{2,13} bis(5-*tert*-butyl-2-hydroxy-3-hydroxymethylphenyl)methane¹³ and UCl_4 ²³ were prepared by published methods. Elemental

Table 2 Crystal data and structure refinement details

	1	2	3
Chemical formula	C ₄₃ H ₄₈ Cl ₄ N ₄ O ₂ U	C ₉₁ H ₁₀₁ Cl ₄ N ₉ O ₄ U	C ₅₄ H ₆₁ Cl ₃ N ₄ O ₃ U
<i>M</i> /g mol ⁻¹	1032.68	1764.64	1158.45
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	11.9036(8)	30.390(3)	9.4648(10)
<i>b</i> /Å	12.0479(6)	15.5898(16)	14.3274(12)
<i>c</i> /Å	16.0063(12)	20.2637(11)	38.870(3)
<i>a</i> °	106.175(4)	90	90
<i>β</i> °	97.611(3)	112.651(5)	95.906(6)
<i>γ</i> °	92.191(4)	90	90
<i>V</i> /Å ³	2178.4(2)	8859.9(13)	5243.0(8)
<i>Z</i>	2	4	4
<i>μ</i> (MoKα)/mm ⁻¹	4.010	2.006	3.293
<i>T</i> /K	100(2)	100(2)	100(2)
Number of data collected	14969	27657	24055
Number of unique data	7631	7909	7839
Number of "observed" data [<i>I</i> > 2σ(<i>I</i>)]	6373	3751	4597
<i>R</i> _{int}	0.057	0.073	0.104
Number of parameters	481	525	595
<i>R</i> ₁ ^a	0.043	0.085	0.068
<i>wR</i> ₂ ^b	0.095	0.173	0.115

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

analyses were performed by Analytische Laboratorien at Lindlar (Germany).

Synthesis

[UCl₄(L¹)]·2py, 1. (a) A mixture of UCl₄ (32.2 mg, 0.0846 mmol) and [3.1.3.1] (30.0 mg, 0.0423 mmol) in pyridine (8 mL) was stirred at 80 °C for 24 h. The light green solution deposited yellow crystals of **1**. These were filtered off and desolvated upon drying under vacuum to give a yellow microcrystalline powder of [UCl₄(L¹)] (56.0 mg, 76%). (Found: C, 45.46; H, 4.48; N, 3.34. C₃₃H₃₈Cl₄N₂O₂U requires C, 45.31; H, 4.35; N, 3.20).

(b) By using the same procedure as in (a), a mixture of UCl₄ (21.5 mg, 0.0565 mmol) and [3.1.3.1.3.1] (20.0 mg, 0.0188 mmol) in pyridine (8 mL) gave [UCl₄(L¹)] (40.5 mg, 82%).

(c) By using the same procedure as in (a), a mixture of UCl₄ (21.5 mg, 0.0565 mmol) and [3.1.3.1.3.1.3.1] (20.0 mg, 0.0141 mmol) in pyridine (8 mL) gave [UCl₄(L¹)] (42.0 mg, 85%).

(d) By using the same procedure as in (a), a mixture of UCl₄ (6.1 mg, 0.0161 mmol) and bis(5-*tert*-butyl-2-hydroxy-3-hydroxymethylphenyl)methane (6.0 mg, 0.0161 mmol) in pyridine (1 mL) gave [UCl₄(L¹)] (12.2 mg, 87%).

In each of these preparations, the crystals collected before drying under vacuum were found by X-ray diffraction analysis to be those of the pyridine solvate **1**.

[UCl₂(L²)₂]Cl₂·5py, 2. A mixture of UCl₄ (2.7 mg, 0.0071 mmol) and [3.1.3.1] (5.0 mg, 0.0071 mmol) in pyridine (1 mL) was stirred at 110 °C for 3 days. In addition to the yellow crystals of **1** which were deposited after 24 h, a small quantity of orange crystals of **2** was obtained.

[UCl₃(L²)]·2py, 3. A mixture of UCl₄ (22.2 mg, 0.0584 mmol) and [3.1.1.3.1.1] (30.0 mg, 0.0292 mmol) in pyridine (8 mL) was stirred at 80 °C for 24 h. The light green solution deposited yellow crystals of **3**. These were filtered off and desolvated upon drying under vacuum to give a yellow microcrystalline powder of [UCl₃(L²)] (49.0 mg, 84%). (Found: C, 52.55; H, 5.05; N, 3.00. C₄₄H₅₁Cl₃N₃O₃U requires C, 52.83; H, 5.10; N, 2.80).

Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer²⁴ using graphite-monochromated Mo-Kα

radiation (λ 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.²⁵ The structures were solved by Patterson map interpretation (**1**) or by direct methods (**2** and **3**) with SHELXS-97²⁶ and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on *F*² with SHELXL-97.²⁶ Absorption effects were corrected empirically with the program DELABS from PLATON.²⁷ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced at calculated positions and were treated as riding atoms with a displacement parameter equal to 1.2 (CH, CH₂) or 1.5 (CH₃) times that of the parent atom. Crystal data and structure refinement parameters are given in Table 2. The molecular plots were drawn with SHELXTL.²⁸ All calculations were performed on a Silicon Graphics R5000 workstation.

CCDC reference numbers 205829–205831.

See <http://www.rsc.org/suppdata/dt/b3/b302809g/> for crystallographic data in CIF or other electronic format.

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