Uranyl Complexes as Scaffolding or Spacers for Cucurbit[6]uril Molecules in Homo- and Heterometallic Species, Including a Novel Uranyl-Lanthanide Complex

Pierre Thuéry

Uranyl Complexes as Scaffolding or Spacers for Cucurbit[6]uril Molecules in Homo- and Heterometallic Species, Including a Novel Uranyl–Lanthanide Complex

Pierre Thuéry,*[a]

[a] NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France
E-mail: pierre.thuery@cea.fr
http://iramis.cea.fr/nimbe/

Abstract. Reaction of uranyl nitrate with cucurbit[6]uril (CB6) and carboxylic or sulfonic acid ligands under hydrothermal conditions and in the presence of additional metal cations (K^I or Ce^{III}) or co-solvents provided four complexes which were crystallographically characterized. $[(UO_2)_2K_2(CB6)(adc)_2(NO_3)_2(H_2O)_2] \cdot 5H_2O$ (**1**), where H_2adc is 1,3-adamantanedicarboxylic acid, crystallizes in the form of a central $K_2(CB6)^{2+}$ column surrounded by two one-dimensional (1D) polymeric $UO_2(adc)(NO_3)^-$ chains attached to the column by nitrate bridges, with a perfect match of the repeat lengths in the two subunits. The longer 1,3-adamantanediacetic acid (H_2adac) gives the complex $[(UO_2)_2(adac)_2(HCOOH)_2] \cdot CB6 \cdot 6H_2O$ (**2**) in which the 1D uranyl-containing polymer and columns of CB6 molecules form a layered arrangement held by weak CH···O hydrogen bonds. The complex formed with the di-potassium salt of methanedisulfonic acid (K_2mds), $[(UO_2)_2K_2(CB6)(mds)_2(OH)_2(H_2O)_8] \cdot 4H_2O$ (**3**), is a 1D polymer in which $K_2(CB6)^{2+}$ units are connected to one another by doubly hydroxide-bridged uranyl dimers in which the disulfonates are terminal, chelating ligands; connection between the two subunits is solely through potassium oxo-bonding to uranyl. The complex $[(UO_2)_2Ce_2(CB6)(C_2O_4)_3(NO_3)_4(H_2O)_6] \cdot 2H_2O$ (**4**) is a 1D polymer containing bridging oxalate ligands formed in situ, in which CB6 is coordinated to the lanthanide cations only; one nitrate and one water ligands hydrogen bonded to each other are included in the CB6 cavity, with the possible occurrence of interactions between nitrate oxygen atoms and ureido carbon atoms.

Introduction

The complexing properties of cucurbit[n]urils (CBn, n = 5–8)[1] toward f-element cations, either lanthanides (4f) or actinides (5f) have attracted much interest in recent years. In the case of actinides, one incentive for such work, besides its relevance for structural inorganic chemistry and metal–organic polymer studies, is the potential of these macrocycles for removal of uranyl, or more generally actinyl, cations from nuclear wastes.[2] Cucurbiturils proved to be efficient ligands for lanthanide cations,[1j,3] which are generally bound to at least one (most often two or three) carbonyl groups, although examples of second sphere coordination mediated by water molecules or organic ligands have also been found.[3h,j,k] Both first- and second-sphere complexes have been described with thorium(IV)[4] and uranyl cations,[5] and the first polyrotaxanes including uranyl-containing threads and CB6 macrocyclic beads were also recently reported.[6] An interesting case is that in which uranyl cations are reacted with CBs in the presence of carboxylic or sulfonic acids: coordination to both species of ligands occurs in some cases,[5f,g,i] but a frequent outcome is coordination of uranyl to the carboxylate or sulfonate ligands only, the CB molecule being either free or complexed to alkali or alkaline-earth metal cations, or involved in weak interactions with ammonium cations.[5g–j] In the latter cases, association of the uranyl complex subunit, sometimes polymeric, and the macrocycles, through ion-dipole or hydrogen bonding interactions, or coordination bonds mediated by alkali or alkaline-earth cations, has been shown to be a source of original architectures. In particular, the tendency of uranyl-containing coordination polymers[7] to give undulating layers matches with the propensity of CB6 to pack into columns, which results in assemblies in which the former are draped around the latter.[5g] The present work reports novel results obtained in this family of uranyl complexes with mixed ligands. Although many carboxylic and sulfonic acids have been tried in the present as well as in previous experiments, most did not

give any exploitable crystalline material, and the results presented here involve some very different ligands which allowed to grow crystals suitable for X-ray crystallography. These ligands are oxalic acid (generated in situ), 1,3-adamantanedicarboxylic acid (H_2adc), 1,3-adamantanediacetic acid (H_2adac), and the di-potassium salt of methanedisulfonic acid (K_2mds). Oxalate is a very common ligand for uranyl ions, with more than 150 crystal structures reported in the Cambridge Structural Database (CSD, Version 5.38),[8] but the adamantane-based dicarboxylates have been the subject of few reports.[9] Sulfonates are not frequently used to generate uranyl–organic polymeric assemblies,[5h,i,k,l,10] and there is no case reported with the simplest disulfonate, mds^{2-}. While heterometallic complexes uniting uranyl and lanthanide cations are generally not extremely common,[10a,11] several such species were found that involve CB6 ligands,[5c,k] which show that, in the additional presence of a sulfonate ligand, the lanthanide cation binds preferentially to CB6, and the uranyl cation to the sulfonate groups.[5k] A novel uranyl–lanthanide–CB6 complex is described herein, the first to involve a carboxylate co-ligand.

Results and Discussion

The asymmetric unit in the complex $[(UO_2)_2K_2(CB6)(adc)_2(NO_3)_2(H_2O)_2]\cdot5H_2O$ (**1**) contains one uranyl and one potassium cations, one adc^{2-} and one nitrate ligand, and half a centrosymmetric CB6 molecule (Figure 1). The uranium atom is chelated by two carboxylate groups from two adc^{2-} anions and one nitrate ion, its environment being thus hexagonal bipyramidal [U–O(oxo) bond lengths 1.783(4) and 1.774(4) Å, U–O(carboxylate) 2.415(4)– 2.485(4) Å, U–O(nitrate) 2.501(4) and 2.517(4) Å]. A simple, single-stranded one-dimensional (1D) polymer running along the *a* axis is thus generated, which differs from the ribbon- or braid-shaped ones previously described in homometallic uranyl complexes including coordinated solvent

3
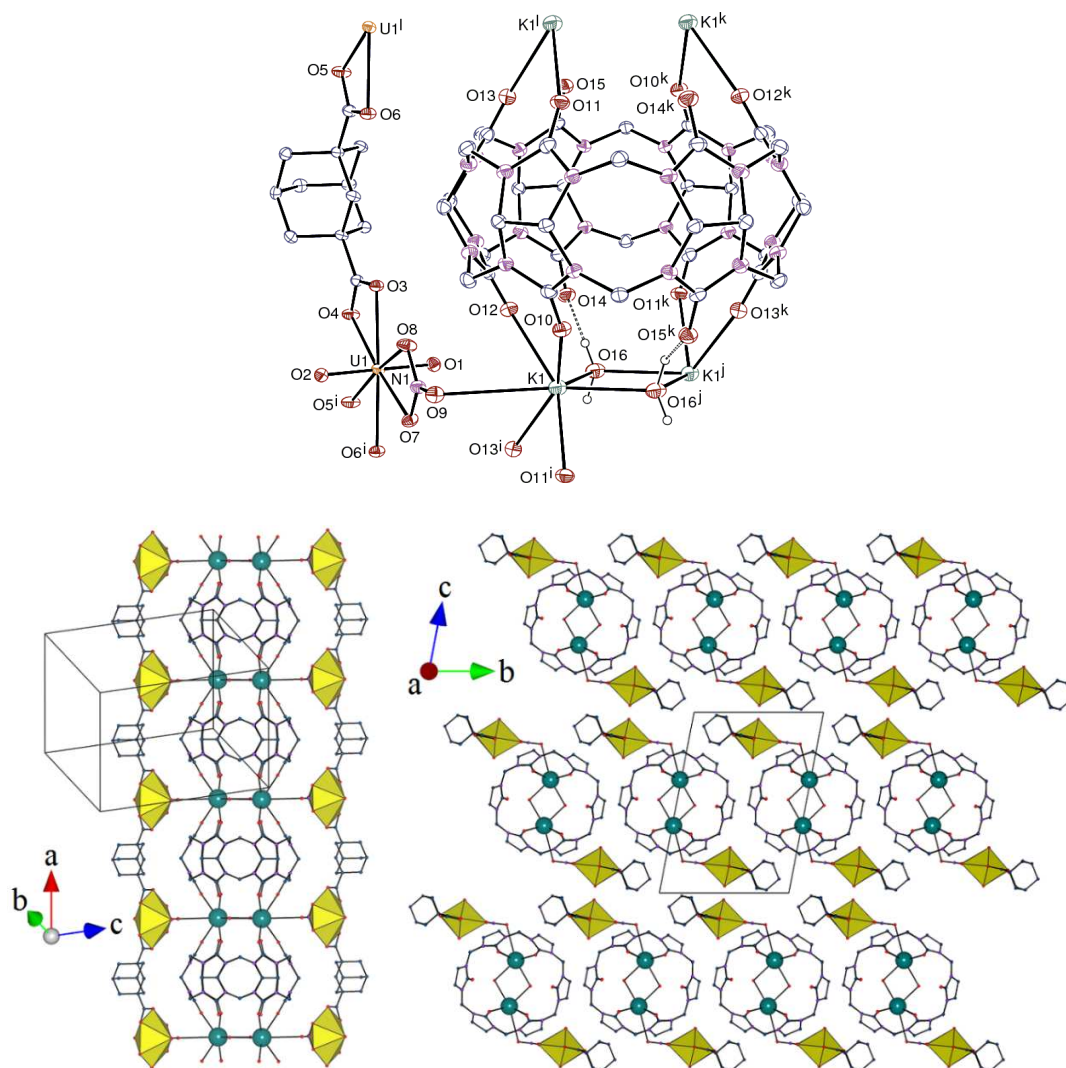
Figure 1. Top: view of compound **1**. Displacement ellipsoids are drawn at the 30% probability level. The solvent molecules and the carbon-bound hydrogen atoms are omitted. The hydrogen bonds are shown as dashed lines. Symmetry codes: i = x + 1, y, z; j = 1 − x, 2 − y, 1 − z; k = −x, 2 − y, 1 − z; l = x − 1, y, z. Bottom: views of the 1D polymer (left) and the packing parallel to the chain axis (right); the uranium coordination polyhedra are colored yellow and potassium atoms are shown as blue spheres, solvent molecules and hydrogen atoms are omitted.

molecules (water, *N,N*-dimethylformamide or *N*-methyl-2-pyrrolidone).[9a,b] Two potassium cations bridged by two water molecules are each bound to four carbonyl groups from two CB6

molecules, thus forming a 1D polymer running along the *a* axis. A similar arrangement, with water replaced by hydroxide bridges, was found in the potassium complex of CB6;[12] the K–O(carbonyl) bond lengths of 2.689(4)–2.764(4) Å in **1** are slightly shorter than those in the latter complex, 2.784(3) and 2.794(3) Å. The K–O(water) bond lengths of 2.693(5) and 2.729(5) Å are comparable to the average value of 2.82(12) Å for the 262 cases of bridging water molecules reported in the CSD. A seventh, longer contact between potassium and the nitrate oxygen atom O9 not bound to uranyl, at 3.387(5) Å, makes for a distorted capped trigonal prismatic environment, with the loosely coordinated atom O9 in the capping position. The water molecules are hydrogen bonded to carbonyl oxygen atoms [O···O distances 2.797(6) and 2.805(6) Å, O–H···O angles 160 and 141°]. The CB6 molecule presents some ellipsoidal distorsion, with O···O distances between oxygen atoms facing one another across the portal of 6.419(6), 6.773(6) and 7.439(6) Å, the longest one corresponding to the uncoordinated oxygen atoms. Both the $[UO_2(adc)(NO_3)]^-$ anionic uranyl-containing polymer and the cationic $[K_2(CB6)(H_2O)_2]^{2+}$ columns run side-by-side with a 2:1 stoichiometry, and the perfect size match between the repeat units of both (equal to the *a* axis unit length) ensures that the uranium···uranium and potassium···potassium distances along the axis are equal, these atoms being located in planes perpendicular to the polymer chain axis. This results in the CB6 columns appearing to be propped by uranyl-based scaffolding, the connection between these subunits being through weak potassium bonding to nitrate. Analysis of the Hirshfeld surface[13] calculated with CrystalExplorer[14] shows that, apart from this potassium–nitrate bonding, there is no interaction exceeding dispersion between the two subunits. The packing is such that layers of columns stacked in a bump-to-hollow fashion lie parallel to (0 0 1), adjacent layers along the *c* axis facing each other through the $[UO_2(adc)(NO_3)]^-$ chains. Two complexes of terbium(III) with adc^{2-} and CB6 were previously described, which crystallize either as a three-

dimensional (3D) framework, or an assembly uniting alternate layers of CB6 and a planar, two-dimensional (2D) terbium–adc^{2-} polymer, and which differ from the present complex by the direct coordination of Tb^{III} to CB6 in the first case, and the absence of bonding between the two subunits in the second.[3r]

Replacement of 1,3-adamantanedicarboxylic acid by 1,3-adamantanediacetic acid, in which the two acid groups are separated by five carbon atoms instead of three, provides the complex
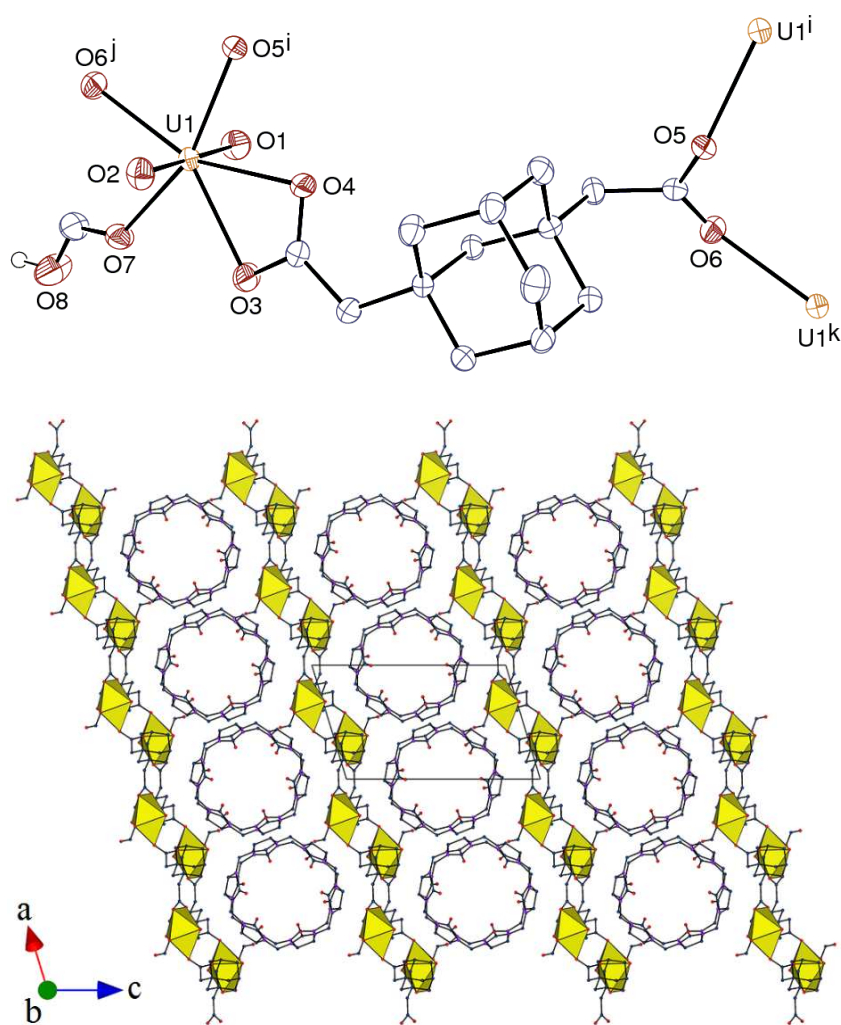

Figure 2. Top: view of the uranyl complex in **2**. Displacement ellipsoids are drawn at the 50% probability level. The solvent molecules and carbon-bound hydrogen atoms are omitted. Symmetry codes: i = −x, 1 − y, −z; j = x + 1, y, z; k = x − 1, y, z. Bottom: packing showing the alternate layers along the c axis.

[(UO$_2$)$_2$(adac)$_2$(HCOOH)$_2$]·CB6·6H$_2$O (**2**), in which formic acid results from *N,N*-dimethylformamide (DMF) hydrolysis, a frequent occurrence in solvo-hydrothermal syntheses.[5g,h,j,9c] The asymmetric unit in **2** contains one uranyl cation, one adac^{2-} ligand and half a centrosymmetric CB6 molecule (Figure 2). The uranyl ion is bound to one chelating carboxylate group, two oxygen atoms from two μ$_2$-κ^1*O*:κ^1*O'*-bridging carboxylate groups from two more ligands and a monodentate formic acid molecule [U–O(oxo) bond lengths 1.779(4) and 1.782(4) Å, U–O(carboxylate) 2.312(4)–2.447(4) Å]. Both uranium and adac^{2-} are thus three-fold nodes and a ribbon-shaped 1D polymer parallel to the *a* axis is formed, which is similar to that found in [UO$_2$(adac)(NMP)] (NMP = *N*-methyl-2-pyrrolidone).[9c] The CB6 molecules are arranged into columns directed along the *b* axis and, being uncomplexed, they are less distorted than in **1**, with O···O distances between oxygen atoms facing one another across the portal of 6.903(7), 6.909(7) and 7.013(8) Å. The uranyl-containing polymers and CB6 columns are arranged in alternate planar layers parallel to (0 0 1), an arrangement analogous to those found in other compounds involving uranyl carboxylates (and also terbium(III) adamantanedicarboxylate[3r]) and CBs.[5g,h] The hydrogen atom of the formic acid ligand forms a hydrogen bond with a lattice water molecule [O···O distance 2.767(9) Å, O–H···O angle 146°], and analysis of the Hirshfeld surface shows that weak CH···O hydrogen bonds[15] link the CB6 molecule and the uranyl complex subunit, with H···O distances as short as 2.31 Å for that involving the uncoordinated formic acid atom O8.

A heterometallic complex containing uranyl and potassium cations was obtained with the methanedisulfonate dianion, [(UO$_2$)$_2$K$_2$(CB6)(mds)$_2$(OH)$_2$(H$_2$O)$_8$]·4H$_2$O (**3**). The asymmetric unit contains one of each metal cation, one mds^{2-} ligand and half a centrosymmetric CB6 molecule (Figure 3). The uranyl cation is chelated by two sulfonate groups from one ligand and is also bound
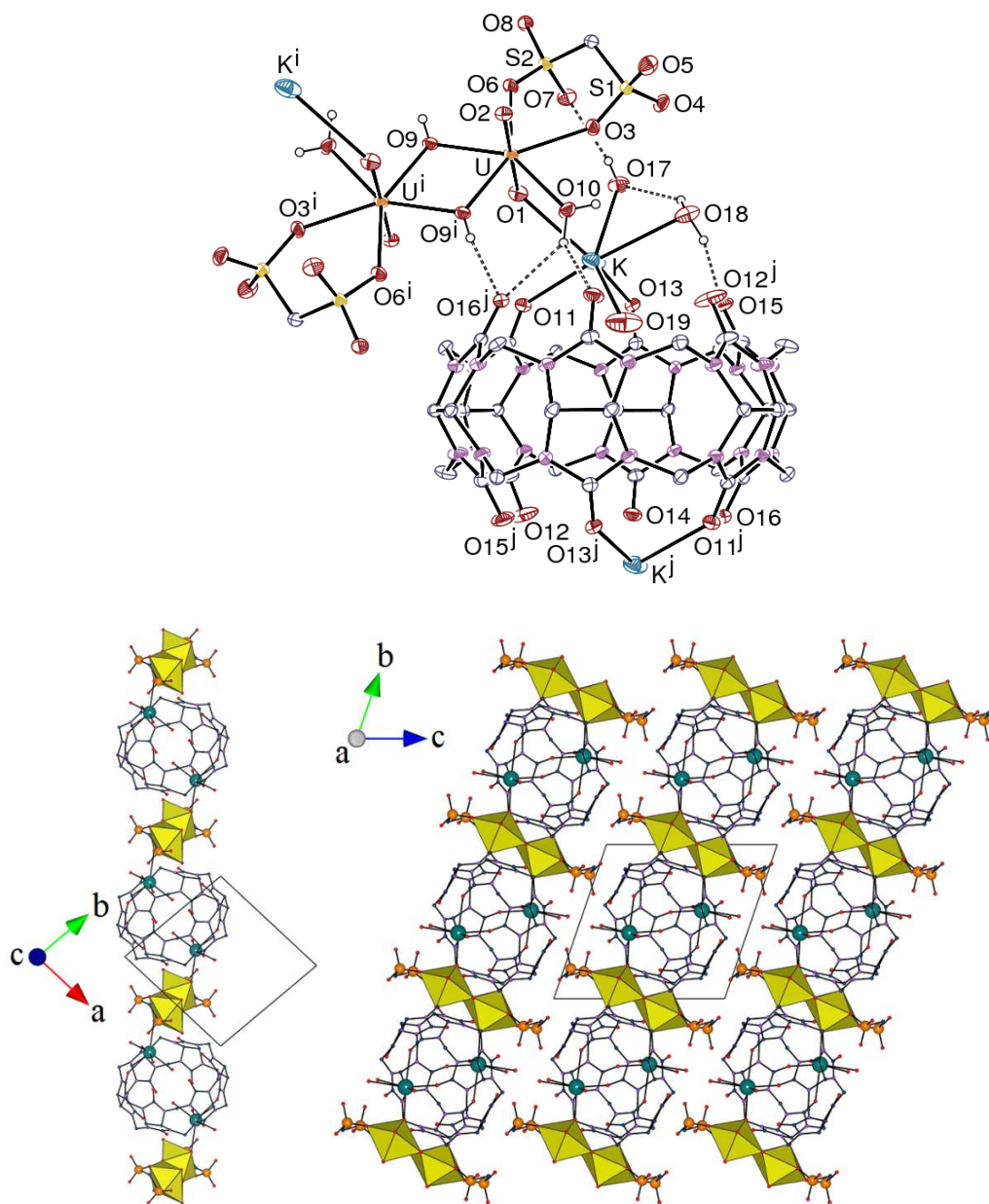
Figure 3. Top: view of compound **3**. Displacement ellipsoids are drawn at the 30% probability level. The solvent molecules and the carbon-bound hydrogen atoms are omitted. Hydrogen bonds are shown as dashed lines. Symmetry codes: i = 1 − x, −y, 1 − z; j = −x, 1 − y, 1 − z. Bottom: views of the 1D polymer (left) and the packing (right); the uranium coordination polyhedra are colored yellow and potassium atoms are shown as blue spheres, solvent molecules and hydrogen atoms are omitted.

to one water molecule and two bridging hydroxide groups, the latter generating a centrosymmetric uranyl dimer. The U–O(oxo) bond lengths of 1.773(3) and 1.777(3) Å are unexceptional, as well as the U–O(sulfonate) bond lengths of 2.393(3) and 2.413(3) Å [average 2.40(4) Å for uranyl–sulfonate bonds reported in the CSD]. The $\{[UO_2(OH)]_2\}^{2+}$ motif is a frequent one, with 42 examples reported in the CSD, and the U–O bond lengths of 2.319(3) and 2.337(3) Å and U–O–U angle of 109.59(11)° match the average values from the literature [2.34(4) Å and 111(3)°]. In contrast to compound **1**, only one potassium cation is bound to two carbonyl groups at each CB6 portal, with however not very different K–O bond lengths [2.576(3) and 2.768(5) Å]. The resulting ellipsoidal distorsion of CB6 is intermediate between those in **1** and **2**, with O···O distances between oxygen atoms facing one another across the portal of 6.556(5), 6.934(7) and 7.056(6) Å. Three water molecules, at 2.659(5)–3.001(5) Å are also bound to potassium, which is also involved in oxo bonding to uranyl, with a K–O1 bond length of 2.934(4) Å that is at the upper end of the range of 2.58–3.08 Å [average 2.76(10) Å] in the 26 similar cases reported in the CSD (some of them involving U^V instead of U^{VI}). Although there is no obvious lengthening of the U=O1 bond length, which would indicate that the K–O1 bond is weak at best, this interaction appears prominently in the Hirshfeld surface (Figure 4). The presence of this oxo bonding and the dimeric nature of the uranyl complex subunit give rise to the formation of a 1D polymer parallel to [1 $\bar{1}$ 0]. The hydroxide anion is involved in an intra-chain hydrogen bond with a carbonyl group [O···O distance 2.702(4) Å, O–H···O angle 170°], as well as the water molecule bound to uranyl (one of the bonds in this case being mediated by a lattice water molecule); one of the water ligands bound to potassium is directed toward the CB6 cavity (O19) and, although its hydrogen atoms have not been found, short O···O contacts of 3.00–3.27 Å indicate that it is probably hydrogen bonded to carbonyl oxygen atoms; the other two water molecules bound to potassium are involved in three intra-chain

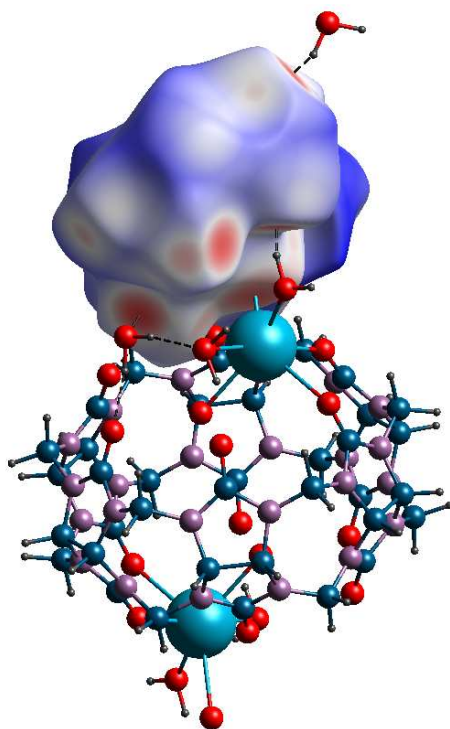hydrogen bonds and, in the case of O17, one inter-chain one [O⋯O distances 2.759(5)–2.933(5) Å, O–H⋯O angles 123–170°].

Figure 4. Hirshfeld surface mapped with d_{norm} of the anionic subunit in complex **3**, showing the oxo bonding interaction of the potassium cation (blue sphere). The hydrogen bonds made by water molecules are shown as dashed lines. The contacts shorter than the van der Waals separation appear as red spots on the surface, the two prominent ones at the forefront corresponding to OH⋯O (right) and CH⋯O (left) hydrogen bonds with neighbouring units (not represented).

The compound $[(UO_2)_2Ce_2(CB6)(C_2O_4)_3(NO_3)_4(H_2O)_6]\cdot 2H_2O$ (**4**) contains oxalate anions formed in situ, a common occurrence in complexes synthesized by hydrothermal methods,[11a,b,16] the corresponding formation pathway having however been elucidated only in some particular cases.[17] The asymmetric unit in **4** contains two uranyl and two cerium(III) cations, three oxalate anions (including two halves of centrosymmetric ones), four nitrate anions and one complete CB6

10

molecule (Figure 5). The two uranyl atoms are chelated by one nitrate and two oxalate anions [U–O(oxo) bond lengths 1.752(3)–1.771(3) Å; U–O(oxalate) 2.425(2)–2.501(3) Å, average 2.47(3) Å;
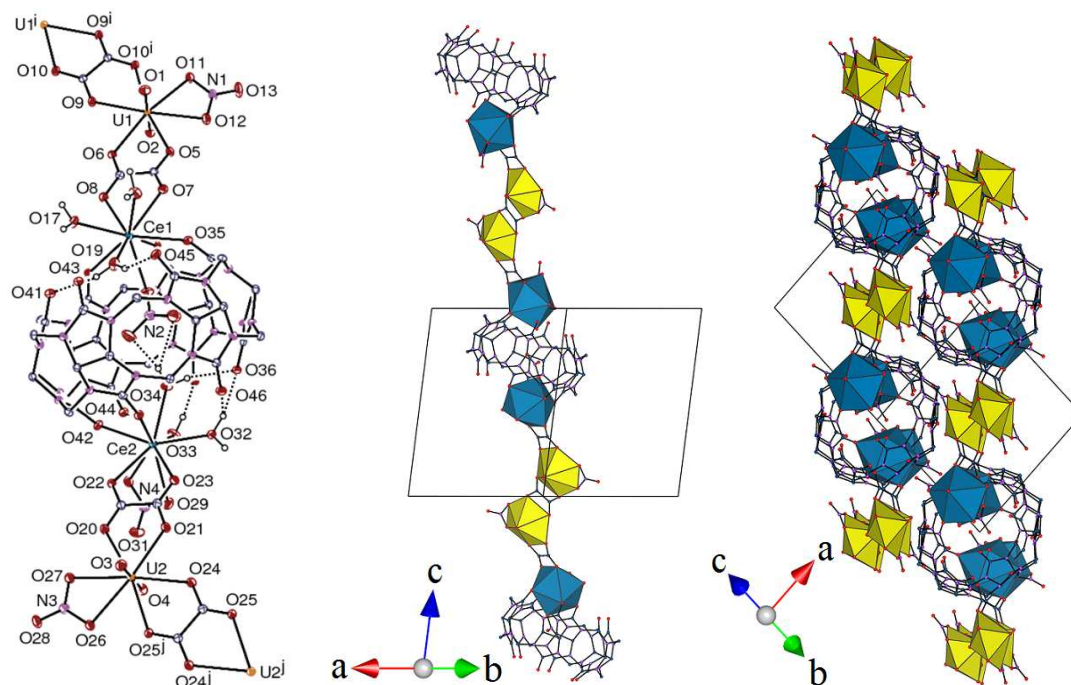

Figure 5. Left: view of compound **4**. Displacement ellipsoids are drawn at the 30% probability level. The solvent molecules and the carbon-bound hydrogen atoms are omitted. Hydrogen bonds are shown as dashed lines. Symmetry codes: i = 1 – x, 1 – y, 2 – z; j = –x – 1, –y, –z – 1. Middle: view of the 1D polymer. Right: view of the packing. The uranium coordination polyhedra are colored yellow and those of cerium blue, solvent molecules and hydrogen atoms are omitted in the last two views.

U–O(nitrate) 2.518(3)–2.558(3) Å, average 2.536(15) Å; the last two ranges are in agreement with the average values for similar motifs in the CSD, 2.45(4) and 2.52(4) Å, respectively]. The centrosymmetric oxalate ligands ensure the formation of uranyl dimers, while the other oxalate anions bridge uranium and cerium cations. The two independent Ce^{III} centres are in slightly different environments since, apart from one chelating oxalate and three water molecules which are common to both, Ce1 is bound to three carbonyl groups from CB6 and one monodentate nitrate anion, while Ce2 is bound to two carbonyl groups and one chelating nitrate. In both cases, the nine-

coordinate environment is capped square antiprismatic, with atoms O14 (nitrate) and O34 (water) in the capping positions. The Ce–O(carbonyl) bond lengths of 2.440(2)–2.656(2) Å fall within the large range measured for Ce bond lengths to CB6, 2.40–2.75 Å.[3a,g,j,k,t] The Ce–O(oxalate) bond lengths of 2.537(3)–2.568(3) Å [average 2.552(12) Å] match the average value of 2.55(5) Å from the CSD. As expected, the Ce–O(nitrate) bond length is shorter for the monodentate group [2.496(3) Å] than for the chelating one [2.609(3) and 2.673(3) Å], both being in agreement with the average values for similar cases in the CSD, 2.50(7) and 2.62(7) Å, respectively. The Ce–O(water) bond lengths span the range 2.457(3)–2.569(3) Å [average 2.50(4) Å, to be compared to 2.53(6) Å from the CSD]. Coordination of two lanthanide cations, one at each portal of CB5, CB6, CB7 or their derivatives, resulting in the formation of polymeric chains, is frequently observed, as are also chains with two bridging lanthanide cations at each portal.[1j,3g,l,n,18] A 1D polymer running along the [2 1 3] axis is formed here also, but the originality of the present structure arises from the incorporation of uranyl oxalate dimers into the chains, which act as spacers for $Ce_2(CB6)^{6+}$ units. It has been shown that, in the presence of perrhenate anions, uranyl–lanthanide heterometallic complexes with CB6 could be obtained, in which both cations are bound to carbonyl groups,[5c] and also that, in the presence of 1,2-ethanedisulfonate, only the lanthanide cation is coordinated to CB6, uranyl being bound to sulfonate, hydroxide and water ligands.[5k] Compound **4** shows that the same trend is found when a dicarboxylate ligand is present, with uranyl preferentially bound to carboxylates, and Ce^{III} to CB6 (with additional bonding to carboxylates). The chains are stacked in a bump-to-hollow fashion, as expected from the bulkiness of CB6. The monodentate nitrate anion bound to Ce1 and one of the water molecules bound to Ce2 are included in the CB6 cavity, the water molecule being involved in an asymmetric, bifurcated hydrogen bond with the two uncoordinated nitrate oxygen atoms [O···O distances 2.727(4) and 2.944(4) Å, O–H···O angles 164

and 134°], and another one with a carbonyl group [3.027(4) Å, 160°]. The position of the nitrate group in the CB6 cavity is probably determined in a large measure by hydrogen bonding to the water ligand, the stronger component of the bifurcated bond being with atom O15. Inclusion of coordinated or free anions in CBs is common and has been reported for nitrate,[3d,j,5k] and also for species as diverse as chloride,[3c,d,4a] acetate,[1d] isonicotinate[3e,f] or perrhenate.[3g,4b,5c] The coordinated nitrate atom O14 (and also to a lesser extent the uncoordinated atom O16) makes several contacts with oxygen, nitrogen and carbon atoms of CB6, in the range 2.7–3.4 Å, the shortest being with a ureido carbon atom at 2.717(5) Å [2.915(5) Å in the case of O16], which is in keeping with the fact that, although the cavity lining of CBs is overall negatively charged,[1b] the bonding of ureido carbon atoms to three electron-withdrawing atoms makes them slightly electropositive,[1f] an effect which may be reinforced by carbonyl groups coordination.[3c,d,19] These shortest contacts made by O14 and O16 with ureido carbon atoms are well apparent on the Hirshfeld surface of the nitrate anion (Figure 6), which confirms their significance. The CB6 molecule presents an ellipsoidal distorsion larger than that in compounds **1**–**3**, with O···O distances between oxygen atoms facing one another across the portal in the range of 6.198(4)–7.796(4) Å. An intricate network of hydrogen bonds involving the coordinated and free water molecules as donors and uranyl, nitrate, carboxylate, carbonyl and water oxygen atoms as acceptors unites the chains into a 3D assembly.
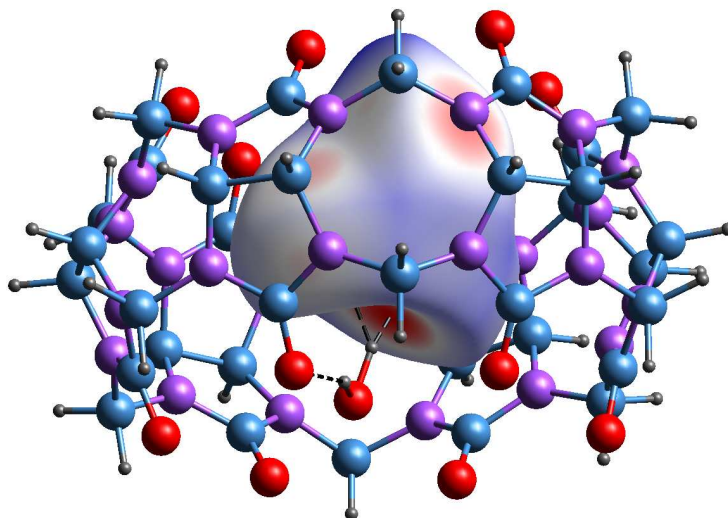
Figure 6. Hirshfeld surface mapped with d_{norm} of the included nitrate anion in complex **4**. The hydrogen bonds made by the included water molecule are shown as dashed lines. The contacts shorter than the van der Waals separation appear as red spots on the surface and correspond to the hydrogen bond and the contacts between O14 (right) and O16 (left) with ureido carbon atoms. The bump at the top of the Hirshfeld surface is due to removal of the coordinated cerium atom.

Conclusions

Previous work has shown that combining cucurbiturils and carboxylic, sulfonic or mineral acids as ligands for uranyl cations provides complexes displaying original and varied structures, with either all components involved in the building of a single complex unit, often multi-dimensional, or formation of separate subunits in the cases in which no direct bonding of uranyl to the macrocycle occurs.[5b–l] The four complexes reported herein, which all involve CB6, constitute an extension of this work to three carboxylates, oxalate, 1,3-adamantanedicarboxylate and 1,3-adamantanediacetate, and the simplest of disulfonates, methanedisulfonate. In no case is there any direct bonding of uranyl to CB6, the latter being bound instead to potassium or cerium cations when present. Complex **1**, with 1,3-adamantanedicarboxylate, displays columns of uranyl

dicarboxylate chains and potassium–CB6 chains running side-by-side and associated to one another through bridging nitrate anions, in which a remarkable feature is the perfect match in length of the repeat units of both chains, resulting in two uranyl-containing strands surrounding each CB6 column as scaffolding. This pattern is disrupted with 1,3-adamantanediacetate in complex **2**, due not only to the absence of potassium ions but also to the longer size of the carboxylate ligand which would not enable the match in length between the two subunits. Instead, 1D uranyl-containing polymers associate with columns of CB6 molecules to form a layered arrangement. In the case of methanedisulfonate (complex **3**), CB6–di-potassium cations are linked to one another by uranyl dimers containing hydroxide bridges and chelating sulfonate ligands, the connection between the subunits being solely through potassium oxo-bonding to uranyl. Complex **4** is a heterometallic complex containing uranyl and cerium(III) cations, in which 1D polymerization arises from the presence of oxalate anions formed in situ. As in previous cases of uranyl–lanthanide heterometallic complexes with sulfonate anions and CB6 molecules,[5k] the macrocycle preferentially coordinates to the lanthanide cation, the uranyl cation being chelated by one nitrate and two oxalate ligands. One nitrate anion and one water molecule, bound to different Ce^{III} ions and hydrogen bonded to each other, are included in the CB6 cavity, an arrangement which may involve interactions between two nitrate oxygen atoms and slightly electropositive ureido carbon atoms.

Experimental Section

General: $UO_2(NO_3)_2 \cdot 6H_2O$ (depleted uranium, R. P. Normapur, 99%), KNO_3, and $Ce(NO_3)_3 \cdot 6H_2O$ were purchased from Prolabo, cucurbit[6]uril pentahydrate was from Fluka, 1,3-adamantanedicarboxylic acid, 1,3-adamantanediacetic acid and the di-potassium salt of methanedisulfonic acid were from Aldrich. Elemental analyses of the crystals could not be

conducted since in all cases their formation was accompanied by the presence of insoluble remnants of cucurbit[6]uril and/or the deposition of amorphous precipitates.

Caution! *Uranium is a radioactive and chemically toxic element, and uranium-containing samples must be handled with suitable care and protection.*

[(UO$_2$)$_2$K$_2$(CB6)(adc)$_2$(NO$_3$)$_2$(H$_2$O)$_2$]·5H$_2$O (1): CB6·5H$_2$O (11 mg, 0.01 mmol), H$_2$adc (11 mg, 0.05 mmol), UO$_2$(NO$_3$)$_2$·6H$_2$O (50 mg, 0.10 mmol), KNO$_3$ (20 mg, 0.20 mmol), and demineralized water (0.8 mL) were placed in a 15 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving light yellow crystals of complex **1** in low yield within two weeks.

[(UO$_2$)$_2$(adac)$_2$(HCOOH)$_2$]·CB6·6H$_2$O (2): CB6·5H$_2$O (11 mg, 0.01 mmol), H$_2$adac (13 mg, 0.05 mmol), UO$_2$(NO$_3$)$_2$·6H$_2$O (25 mg, 0.05 mmol), *N,N*-dimethylformamide (0.3 mL), and demineralized water (1.0 mL) were placed in a 15 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving light yellow crystals of complex **2** in low yield within two weeks.

[(UO$_2$)$_2$K$_2$(CB6)(mds)$_2$(OH)$_2$(H$_2$O)$_8$]·4H$_2$O (3): CB6·5H$_2$O (11 mg, 0.01 mmol), K$_2$mds (25 mg, 0.10 mmol), UO$_2$(NO$_3$)$_2$·6H$_2$O (50 mg, 0.10 mmol), and demineralized water (1.5 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure, giving light yellow crystals of complex **3** in low yield within one week.

[(UO₂)₂Ce₂(CB6)(C₂O₄)₃(NO₃)₄(H₂O)₆]·2H₂O (4): $[(UO_2)_2Ce_2(CB6)(C_2O_4)_3(NO_3)_4(H_2O)_6]\cdot 2H_2O$ **(4):** CB6·5H₂O (11 mg, 0.01 mmol), α-cyclodextrin (20 mg, 0.02 mmol), UO₂(NO₃)₂·6H₂O (50 mg, 0.10 mmol), Ce(NO₃)₃·6H₂O (43 mg, 0.10 mmol), and demineralized water (1.5 mL) were placed in a 15 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving light yellow crystals of complex **4** in low yield within one month.

Crystallography: The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[20] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were introduced into glass capillaries with a protective coating of Paratone-N oil (Hampton Research). The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of φ- and ω-scans with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[21] Absorption effects were corrected empirically with the program SCALEPACK.[21] The structures were solved either by Patterson map interpretation (**3**) or direct methods (**4**) with SHELXS,[22] or by intrinsic phasing with SHELXT[23] (**1** and **2**), expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F^2 with SHELXL.[22] All non-hydrogen atoms were refined with anisotropic displacement parameters. In compound **1**, one water molecule (O18) is disordered over two positions which were refined with occupancy parameters constrained to sum to unity, and another one (O19) was given an occupancy factor of 0.5 in order to retain an acceptable displacement parameter. The hydrogen atom of the carboxylic group in **2**, that of the hydroxyl group in **3** and, when possible, the hydrogen atoms bound to water oxygen atoms were retrieved from difference Fourier maps (some of them were not found for **1**, **2** and **3**), and the carbon-bound hydrogen atoms were introduced at calculated positions; all hydrogen atoms were treated as riding atoms with an isotropic displacement

parameter equal to 1.2 times that of the parent atom. Some voids in the lattices of **1** and **2** likely indicate the presence of other, unresolved water solvent molecules. Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3[24] and the packings with VESTA.[25]

CCDC-1538211−1538214 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1 Crystal data and structure refinement details

	1	2	3	4
Empirical formula	$C_{60}H_{78}K_2N_{26}O_{37}U_2$	$C_{66}H_{88}N_{24}O_{34}U_2$	$C_{38}H_{66}K_2N_{24}O_{42}S_4U_2$	$C_{42}H_{52}Ce_2N_{28}O_{48}U_2$
M (g mol^{-1})	2309.74	2237.66	2213.65	2473.42
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.9856(5)	11.8996(5)	12.1522(4)	13.1138(5)
b (Å)	12.8984(7)	12.3665(3)	12.2334(5)	16.6700(7)
c (Å)	17.0795(9)	17.2789(8)	12.7639(4)	16.7399(7)
α (°)	77.465(2)	97.615(3)	70.510(2)	91.081(2)
β (°)	83.433(3)	101.055(2)	83.939(2)	100.123(2)
γ (°)	67.842(3)	118.017(2)	81.505(2)	109.057(2)
V (Å^3)	1987.50(19)	2129.12(16)	1765.93(11)	3393.6(2)
Z	1	1	1	2
ρ_{calcd} (g cm^{-3})	1.930	1.745	2.082	2.421
μ(Mo-K$_\alpha$) (mm^{-1})	4.284	3.898	4.935	6.213
$F(000)$	1138	1108	1084	2368
Reflections collected	115449	122240	100537	216173
Independent reflections	7543	8089	9110	20695
Observed reflections [$I > 2\sigma(I)$]	6964	7524	8530	16532
R_{int}	0.032	0.045	0.064	0.063
Parameters refined	587	568	505	1099
R_1	0.035	0.039	0.039	0.033
wR_2	0.096	0.102	0.107	0.078
S	1.115	1.198	1.045	1.033
$\Delta\rho_{min}$ (e Å^{-3})	−1.08	−1.26	−2.56	−2.18
$\Delta\rho_{max}$ (e Å^{-3})	2.85	2.20	3.00	1.71

References

[1]   a) W. A. Freeman, W. L. Mock, N. Y. Shih, *J. Am. Chem. Soc.* **1981**, *103*, 7367–7368; b) J. W. Lee, S. Samal, N. Selvapalam, H. J. Kim, K. Kim, *Acc. Chem. Res.* **2003**, *36*, 621–630; c) J. Lagona, P. Mukhopadhyay, S. Chakrabarti, L. Isaacs, *Angew. Chem., Int. Ed.* **2005**, *44*, 4844–4870; d) H. Cong, Q. J. Zhu, S. F. Xue, Z. Tao, G. Wei, *Chinese Sci. Bull.* **2010**, *55*, 3633–3640; e) W. M. Nau, M. Florea, K. I. Assaf, *Isr. J. Chem.* **2011**, *51*, 559–577; f) D. Bardelang, K. A. Udachin, D. M. Leek, J. C. Margeson, G. Chan, C. I. Ratcliffe, J. A. Ripmeester, *Cryst. Growth Des.* **2011**, *11*, 5598–5614; g) E. Masson, X. Ling, R. Joseph, L. Kyeremeh-Mensah, X. Lu, *RSC Adv.* **2012**, *2*, 1213–1247; h) J. Lü, J. X. Lin, M. N. Cao, R. Cao, *Coord. Chem. Rev.* **2013**, *257*, 1334–1356; i) X. L. Ni, X. Xiao, H. Cong, L. L. Liang, K. Cheng, X. J. Cheng, N. N. Ji, Q. J. Zhu, S. F. Xue, Z. Tao, *Chem. Soc. Rev.* **2013**, *42*, 9480–9508; j) X. L. Ni, S. F. Xue, Z. Tao, Q. J. Zhu, L. F. Lindoy, G. Wei, *Coord. Chem. Rev.* **2015**, *287*, 89–113; k) K. I. Assaf, W. M. Nau, *Chem. Soc. Rev.* **2015**, *44*, 394–418.

[2]   a) M. Sundararajan, V. Sinha, T. Bandyopadhyay, S. K. Ghosh, *J. Phys. Chem. A* **2012**, *116*, 4388–4395; b) L. Shao, X. Wang, Y. Ren, S. Wang, J. Zhong, M. Chu, H. Tang, L. Luo, D. Xie, *Chem. Eng. J.* **2016**, *286*, 311–319.

[3]   See, for example: a) D. G. Samsonenko, J. Lipkowski, O. A. Gerasko, A. V. Virovets, M. N. Sokolov, V. P. Fedin, J. G. Platas, R. Hernandez-Molina, A. Mederos, *Eur. J. Inorg. Chem.* **2002**, 2380–2388; b) O. A. Gerasko, M. N. Sokolov, V. P. Fedin, *Pure Appl. Chem.* **2004**, *76*, 1633–1646; c) J. X. Liu, L. S. Long, R. B. Huang, L. S. Zheng, *Cryst. Growth Des.* **2006**, *6*, 2611–2614; d) J. X. Liu, L. S. Long, R. B. Huang, L. S. Zheng, *Inorg. Chem.* **2007**, *46*, 10168–10173; e) O. A. Gerasko, E. A. Mainicheva, M. I. Naumova, O. P.

Yurjeva, A. Alberola, C. Vicent, R. Llusar, V. P. Fedin, *Eur. J. Inorg. Chem.* **2008**, 416–424; f) O. A. Gerasko, E. A. Mainicheva, M. I. Naumova, M. Neumaier, M. M. Kappes, S. Lebedkin, D. Fenske, V. P. Fedin, *Inorg. Chem.* **2008**, *47*, 8869–8880; g) P. Thuéry, *Inorg. Chem.* **2009**, *48*, 4497–4513; h) P. Thuéry, *Inorg. Chem.* **2010**, *49*, 9078–9085; i) P. Thuéry, *Inorg. Chem.* **2011**, *50*, 10558–10560; j) P. Thuéry, *Cryst. Growth Des.* **2012**, *12*, 1632–1640; k) P. Thuéry, *CrystEngComm* **2012**, *14*, 8128–8136; l) L. L. Liang, Y. Zhao, Y. Q. Zhang, Z. Tao, S. F. Xue, Q. J. Zhu, J. X. Liu, *CrystEngComm* **2013**, *15*, 3943–3950; m) X. J. Cheng, L. L. Liang, K. Chen, N. N. Ji, X. Xiao, J. X. Zhang, Y. Q. Zhang, S. F. Xue, Q. J. Zhu, X. L. Ni, Z. Tao, *Angew. Chem. Int. Ed.* **2013**, *52*, 7252–7255; n) Y. Zhao, L. L. Liang, K. Chen, T. Zhang, X. Xiao, Y. Q. Zhang, Z. Tao, S. F. Xue, Q. J. Zhu, *CrystEngComm* **2013**, *15*, 7987–7998; o) M. Ren, D. Pinkowicz, M. Yoon, K. Kim, L. M. Zheng, B. K. Breedlove, M. Yamashita, *Inorg. Chem.* **2013**, *52*, 8342–8348; p) F. F. da Silva, C. A. F. de Oliveira, E. H. L. Falcão, J. Chojnacki, J. L. Nevesa, S. Alves Jr., *Dalton Trans.* **2014**, *43*, 5435–5442; q) J. J. Zhou, X. Yu, Y. C. Zhao, X. Xiao, Y. Q. Zhang, S. F. Xue, Z. Tao, J. X. Liu, Q. J. Zhu, *CrystEngComm* **2014**, *16*, 10674–10680; r) P. Thuéry, *J. Solid State Chem.* **2015**, *227*, 265–272; s) N. Rawat, A. Kar, A. Bhattacharyya, A. Rao, S. K. Nayak, C. Nayak, S. N. Jha, D. Bhattacharyya, B. S. Tomar, *Dalton Trans.* **2015**, *44*, 4246–4258; t) B. Yang, Z. Z. Gao, J. H. Lu, Q. J. Zhu, S. F. Xue, Z. Tao, T. J. Prior, C. Redshaw, G. Wei, X. Xiao, *CrystEngComm* **2016**, *18*, 5028–5035.

[4] a) D. G. Samsonenko, M. N. Sokolov, O. A. Gerasko, A. V. Virovets, J. Lipkowski, D. Fenske, V. P. Fedin, *Russ. Chem. Bull., Int. Ed.* **2003**, *52*, 2132–2139; b) P. Thuéry, *Eur. J. Inorg. Chem.* **2015**, 2037–2040.

[5] a) O. A. Gerasko, D. G. Samsonenko, A. A. Sharonova, A. V. Virovets, J. Lipkowski, V. P. Fedin, *Russ. Chem. Bull.* **2002**, *51*, 346–349; b) P. Thuéry, *Cryst. Growth Des.* **2008**, *8*,

4132–4143; c) P. Thuéry, *Inorg. Chem.* **2009**, *48*, 825–827; d) P. Thuéry, *CrystEngComm* **2009**, *11*, 1150–1156; e) P. Thuéry, *Cryst. Growth Des.* **2009**, *9*, 1208–1215; f) P. Thuéry, B. Masci, *Cryst. Growth Des.* **2010**, *10*, 716–725; g) P. Thuéry, *Cryst. Growth Des.* **2011**, *11*, 2606–2620; h) P. Thuéry, *Cryst. Growth Des.* **2011**, *11*, 3282–3294; i) P. Thuéry, *Cryst. Growth Des.* **2011**, *11*, 5702–5711; j) P. Thuéry, *Cryst. Growth Des.* **2012**, *12*, 499–507; k) P. Thuéry, *CrystEngComm* **2012**, *14*, 3363–3366; l) P. Thuéry, J. Harrowfield, *Eur. J. Inorg. Chem.* **2017**, 979–987.

[6]   a) L. Mei, Q. Y. Wu, C. M. Liu, Y. L. Zhao, Z. F. Chai, W. Q. Shi, *Chem. Commun.* **2014**, *50*, 3612–3615; b) L. Mei, L. Wang, C. M. Liu, Y. L. Zhao, Z. F. Chai, W. Q. Shi, *Chem. Eur. J.* **2015**, *21*, 10226–10235; c) L. Mei, L. Wang, L. Y. Yuan, S. W. An, Y. L. Zhao, Z. F. Chai, P. C. Burns, W. Q. Shi, *Chem. Commun.* **2015**, *51*, 11990–11993; d) L. Mei, Z. N. Xie, K. Q. Hu, L. Wang, L. Y. Yuan, Z. J. Li, Z. F. Chai, W. Q. Shi, *Dalton Trans.* **2016**, *45*, 13304–13307.

[7]   a) M. B. Andrews, C. L. Cahill, *Chem. Rev.* **2013**, *113*, 1121–1136; b) T. Loiseau, I. Mihalcea, N. Henry, C. Volkringer, *Coord. Chem. Rev.* **2014**, *266–267*, 69–109; c) J. Su, J. S. Chen, *Struct. Bond.* **2015**, *163*, 265–296.

[8]   C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Crystallogr., Sect. B* **2016**, *72*, 171–179.

[9]   a) J. A. Rusanova, E. B. Rusanov, K. V. Domasevitch, *Acta Crystallogr., Sect. C* **2010**, *66*, m207–m210; b) P. Thuéry, E. Rivière, J. Harrowfield, *Inorg. Chem.* **2015**, *54*, 2838–2850; c) P. Thuéry, J. Harrowfield, *CrystEngComm* **2015**, *17*, 4006–4018.

[10]   a) P. Thuéry, *CrystEngComm* **2012**, *14*, 6369–6373; b) P. Thuéry, *Inorg. Chem.* **2013**, *52*, 435–447; c) P. Thuéry, *CrystEngComm* **2013**, *15*, 2401–2410; d) W. Yang, T. Tian, H. Y.

Wu, Q. J. Pan, S. Dang, Z. M. Sun, *Inorg. Chem.* **2013**, *52*, 2736–2743; e) P. Thuéry, *Eur. J. Inorg. Chem.* **2014**, 58–68.

[11]   a) P. Thuéry, *CrystEngComm* **2008**, *10*, 1126–1128; b) P. Thuéry, *CrystEngComm* **2009**, *11*, 2319–2325; c) P. Thuéry, *Cryst. Growth Des*. **2010**, *10*, 2061–2063; d) P. L. Arnold, E. Hollis, F. J. White, N. Magnani, R. Caciuffo and J. B. Love, *Angew. Chem., Int. Ed*. **2011**, *50*, 887–890; e) J. Diwu, S. Wang, J. J. Good, V. H. DiStefano, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2011**, *50*, 4842–4850; f) K. E. Knope, D. T. de Lill, C. E. Rowland, P. M. Cantos, A. de Bettencourt-Dias and C. L. Cahill, *Inorg. Chem*. **2012**, *51*, 201–206; g) C. Volkringer, N. Henry, S. Grandjean and T. Loiseau, *J. Am. Chem. Soc*. **2012**, *134*, 1275–1283; h) I. Mihalcea, C. Volkringer, N. Henry, T. Loiseau, *Inorg. Chem*. **2012**, *51*, 9610–9618; i) P. L. Arnold, E. Hollis, G. S. Nichol, J. B. Love, J. C. Griveau, R. Caciuffo, N. Magnani, L. Maron, L. Castro, A. Yahia, S. O. Odoh, G. Schreckenbach, *J. Am. Chem. Soc.* **2013**, *135*, 3841–3854; j) P. M. Cantos, S. J. A. Pope, C. L. Cahill, *CrystEngComm* **2013**, *15*, 9039–9051; k) Y. N. Hou, X. T. Xu, N. Xing, F. Y. Bai, S. B. Duan, Q. Sun, S. Y. Wei, Z. Shi, H. Z. Zhang, Y. H. Xing, *ChemPlusChem* **2014**, *79*, 1304–1315; l) P. Thuéry, *Cryst. Growth Des*. **2014**, *14*, 2665–2676; m) P. Thuéry, J. Harrowfield, *Inorg. Chem*. **2015**, *54*, 6296–6305.

[12]   J. Heo, J. Kim, D. Whang, K. Kim, *Inorg. Chim. Acta* **2000**, *297*, 307–312.

[13]   M. A. Spackman, D. Jayatilaka, *CrystEngComm* **2009**, *11*, 19–32.

[14]   S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka, M. A. Spackman, *CrystalExplorer 3.0*, University of Western Australia, 2012.

[15]   a) R. Taylor, O. Kennard, *J. Am. Chem. Soc.* **1982**, *104*, 5063–5070; b) G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441–449.

[16]   See, for example: a) X. Li, R. Cao, D. Sun, Q. Shi, W. Bi, M. Hong, *Inorg. Chem. Commun.* **2003**, *6*, 815–818; b) M. Frisch, C. L. Cahill, *Dalton Trans.* **2005**, 1518–1523; c) B. Li, W. Gu, L. Z. Zhang, J. Qu, Z. P. Ma, X. Liu, D. Z. Liao, *Inorg. Chem.* **2006**, *45*, 10425–10427; d) P. Thuéry, *Polyhedron* **2007**, *26*, 101–106; e) M. Frisch, C. L. Cahill, *J. Solid State Chem.* **2007**, *180*, 2597–2602; f) K. E. Knope, C. L. Cahill, *Inorg. Chem.* **2007**, *46*, 6607–6612; g) K. L. Ziegelgruber, K. E. Knope, M. Frisch, C. L. Cahill, *J. Solid State Chem.* **2008**, *181*, 373–381; h) P. Thuéry, *CrystEngComm* **2008**, *10*, 808–810; i) P. Thuéry, *CrystEngComm* **2010**, *12*, 1905–1911; j) C. E. Rowland, C. L. Cahill, *Inorg. Chem.* **2010**, *49*, 6716–6724; k) P. Thuéry, *Inorg. Chem.* **2011**, *50*, 1898–1904; l) P. Thuéry, *Eur. J. Inorg. Chem.* **2013**, 4563–4573; m) P. Thuéry, E. Rivière, *Dalton Trans.* **2013**, *42*, 10551–10558; n) P. Thuéry, J. Harrowfield, *Inorg. Chem.* **2015**, *54*, 8093–8102; o) N. P. Martin, C. Falaise, C. Volkringer, N. Henry, P. Farger, C. Falk, E. Delahaye, P. Rabu, T. Loiseau, *Inorg. Chem.* **2016**, *55*, 8697–8705.

[17]   a) M. B. Andrews, C. L. Cahill, *CrystEngComm* **2011**, *13*, 7068–7078; b) K. E. Knope, H. Kimura, Y. Yasaka, M. Nakahara, M. B. Andrews, C. L. Cahill, *Inorg. Chem.* **2012**, *51*, 3883–3890.

[18]   See, for example: a) E. A. Mainicheva, A. A. Tripolskaya, O. A. Gerasko, D. Y. Naumov, V. P. Fedin, *Russ. Chem. Bull., Int. Ed.* **2006**, *55*, 1566–1573; b) J. X. Liu, Y. F. Hu, R. L. Lin, W. Q. Sun, X. F. Chu, S. F. Xue, Q. J. Zhu, Z. Tao, *CrystEngComm* **2012**, *14*, 6983–6989; c) X. Qin, X. L. Ni, J. X. Hu, K. Chen, Y. Q. Zhang, C. Redshaw, Q. J. Zhu, S. F. Xue, Z. Tao, *CrystEngComm* **2013**, *15*, 738–744; d) L. L. Liang, X. L. Ni, Y. Zhao, K. Chen, X. Xiao, Y. Q. Zhang, C. Redshaw, Q. J. Zhu, S. F. Xue, Z. Tao, *Inorg. Chem.* **2013**, *52*, 1909–1915; e) C. Y. Shan, W. X. Zhao, Z. Tao, Y. Q. Zhang, *Inorg. Chem.*

Commun. **2016**, *71*, 109–112; f) L. M. Zheng, J. X. Liu, *J. Solid State Chem.* **2017**, *245*, 45–49.

[19]   a) Y. Q. Zhang, Q. J. Zhu, S. F. Xue, Z. Tao, *Molecules* **2007**, *12*, 1325–1333; b) M. Sundararajan, S. K. Ghosh, *J. Incl. Phenom. Macrocycl. Chem.* **2012**, *72*, 437–441.

[20]   R. W. W. Hooft, *COLLECT*, Nonius BV: Delft, The Netherlands, 1998.

[21]   Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.

[22]   G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8.

[23]   G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2015**, *71*, 3–8.

[24]   L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30,* p. 565.

[25]   K. Momma, F. Izumi, *J. Appl. Crystallogr.* **2008**, *41*, 653–658.

Uranyl Complexes as Scaffolding or Spacers for Cucurbit[6]uril Molecules in Homo- and Heterometallic Species, Including a Novel Uranyl–Lanthanide Complex

Pierre Thuéry

Key Topic: Uranyl complexes including cucurbit[6]uril
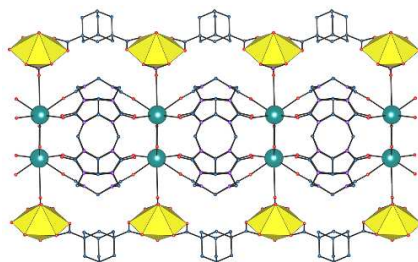
Three dicarboxylic acids and one disulfonic acid were used as ligands to generate four complexes containing uranyl cations and cucurbit[6]uril (CB6) molecules. In no case is uranyl directly bound to CB6, carbonyl groups being coordinated to K^I or Ce^{III} when present. One-dimensional polymers are formed in all cases, the uranyl-containing subunits assuming various roles, in particular as scaffolding for CB6-based columns or spacers in heterometallic complexes.