Reactions of UCl_4 with *t*Bu-Calix[4, 5, and 6]arenes: The First "Non-Uranyl" Calixarene Complexes of Uranium

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Keywords: Alkoxides / Calixarenes / Uranium

The reactions of UCl_4 with *t*Bu-calix[4, 5, and 6]arenes (*t*Bu-calix[*n*]arene = $H_nL[n]$) were used to isolate $[\{UCl(L[4])\}_3O]$ (**1**), $[\{U(L[5])\}_2O]^{2-}$ (**2**), and $[U(H_3L[6])_2]$ (**4**). The dianionic species **2** could be oxidized to its U^{VI} homologue $[\{U(L[5])\}_2O]$ (**3**). In contrast to **1**–**3** that are located around a μ-oxo bridge, **4** can be viewed as a homoleptic alkoxide. **1**–**4** are the first "non-uranyl" calixarene complexes of uranium to be reported.

Introduction

Calixarenes are made of phenolic units linked by methylene bridges into a macrocyclic arrangement.[1] For reasons linked with environmental needs and with the management of nuclear waste solutions, the actinide complexes of these potential polyalkoxide ligands have always attracted special attention from coordination chemists.[2] Research has particularly focussed on the complexes of the uranyl cation $[UO_2]^{2+}$,[3] partly because the special coordination requirements of this cation was thought to be particularly suited to the geometry of calixarenes. However, apart from the work on uranyl cations, surprisingly few complexes of the 5f-metals have been fully characterized. In fact, the thorium compound $[Th_4(HL[8])(H_2L[8])(dmso)_4(OH)_3(OH_2)]$ ($H_nL[n]$ = *t*Bu-calix[*n*]arene, dmso = Me_2SO) is the only "non-uranyl" actinide complex of this family of macrocycles whose crystal structure is available, to date, in the literature.[4] In an attempt to widen the scope of calixarene coordination chemistry to the complexes of uranium at lower oxidation states, we set out to study the reactions of UCl_4 with *t*Bu-calix[4, 5, and 6]arenes. We report herein the synthesis and the X-ray characterization of $[\{UCl(L[4])\}_3O]$ (**1**), $[\{U(L[5])\}_2O]^{2-}$ (**2**), $[\{U(L[5])\}_2O]$ (**3**), and $[U(H_3L[6])_2]$ (**4**). Complexes **1**−**4** are the first "non-uranyl" calixarene complexes of uranium to be reported.

Results and Discussion

When UCl_4 is treated with $H_4L[4]$ or $H_5L[5]$ in pyridine, the pale green solution turns slowly to red. After a few hours of heating the two components at 333 K, the dark red colour turns to black, in the case of $H_4L[4]$, and to a very dark red in the case of $H_5L[5]$. The solutions were allowed to stand, and after a few days, crystals suitable for X-ray crystallography were isolated. The structures were solved and revealed that $[\{UCl(L[4])\}_3O]$ (**1**) and $[\{U(L[5])\}_2O]^{2-}$ (**2**) had been produced by the reaction.

$$3\ UCl_4 + 3\ H_4L[4] \xrightarrow[H_2O]{\text{pyridine}} [\{UCl(L[4])\}_3O] + 12[HNC_5H_5]Cl$$

$$2\ UCl_4 + 2\ H_5L[5] \xrightarrow[H_2O]{\text{pyridine}} [HNC_5H_5]_2[\{U(L[5])\}_2O] + 8[HNC_5H_5]Cl$$

The formation of oxo-alkoxide species such as **1** and **2** is often observed in the process of synthesizing homoleptic alkoxide complexes.[5] The presence of the oxygen atom is usually explained by the hydrolysis of the intermediates by even traces of water or by a number of other possible mechanism e.g. elimination of ether. In our case, the extreme sensitivity of uranium alkoxide to moisture and the absence of any evidence for the chemical transformation of the calixarenes seems to indicate that water is present in the reaction mixture. The syntheses of **1** and **2** were nonetheless very reproducible, and starting from $H_4L[4]$ and $H_5L[5]$, we never managed not to obtain the oxo species. We are currently investigating the reaction of UCl_4 with the sodium salts of calixarenes, which should help to keep the reaction mixture rigorously dry.

Complex **1** is a trinuclear cluster organized around a μ_3-oxo bridge (Figure 1). The two-electron donor O(5) located on the C_3 axis binds the three metal cations in an almost planar fashion (±0.085 Å). This triangular geometry is often encountered in uranium chemistry, and the U(1)−O(5) bond length of 2.224(2) Å is not exceptional when compared to those of other clusters described in the literature.[6] The calixarene is fully deprotonated and all its phenolate groups form σ bonds with the metal center [U−O between 2.042(9) and 2.217(8) Å]. One of the oxygen atoms of the macrocycle [O(2)] helps to maintain the geometry of the cluster by bridging two adjacent uranium atoms [U−O 2.549(8) Å]. One unchanged chloride ligand is still present on each metal cation [U−Cl 2.645(4) Å]. All three U−Cl bonds point in a direction nearly parallel to the C_3 axis. The U−O and U−Cl bond lengths compare well with those found in the literature.[7] Large U−O−C angles of terminal

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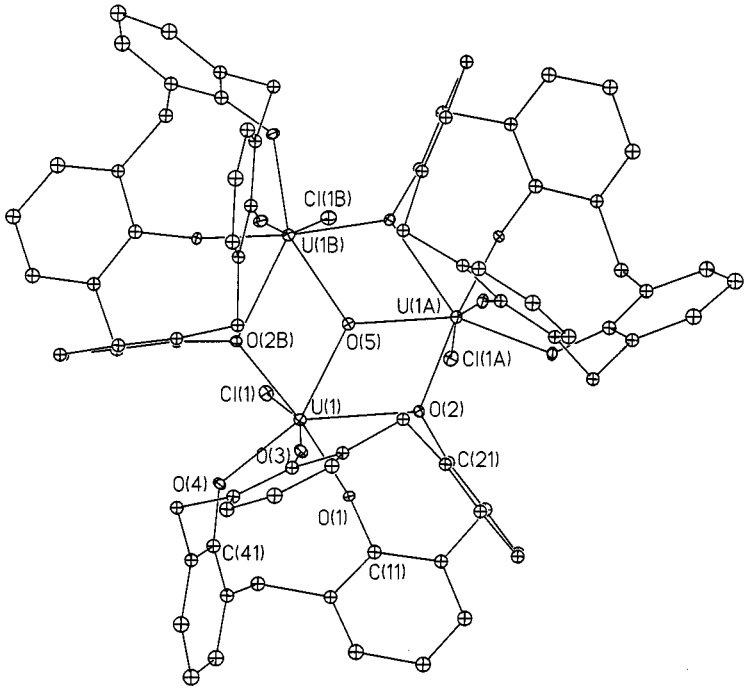

Figure 1. X-ray structure of complex **1** projected along the C_3 axis; all *t*Bu groups and hydrogen atoms or solvent molecules have been omitted for clarity; selected bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: U(1)−O(1) 2.042(9), U(1)−O(2) 2.217(8), U(1)−O(3) 2.08(1), U(1)−O(4) 2.111(9), U(1)−O(5) 2.224(2), U(1)−Cl(1) 2.645(4), U(1)−U(1A) 3.831(2), U(1)−O(2B) 2.549(8); U(1)−O(5)−U(1A) 118.9(2), O(5)−U(1)−Cl(1) 80.9(4), U(1)−O(1)−C(11) 172.3(9), U(1)−O(2)−C(21) 120.4(7), U(1)−O(2A)−C(21A) 132.8(8), U(1)−O(3)−C(31) 171.0(9), U(1)−O(4)−C(41) 130.8(7)

alkoxide ligands are usually interpreted in terms of π-electron donation from the oxygen lone-pair orbitals to the metal ion.[8] These angles range between 130.8(7) and 172(3)° in **1**, which could be associated with substantial π-donation from at least two phenolate groups of the macrocycle [O(1) and O(3)]. However, in the case of bulky ligands such as calixarenes, it seems difficult to draw a line between steric requirements and electronic properties. The three cations share 17 electrons donated by the ligands, formally making **1** a mixed valence complex, with two of its metal centers in the oxidation state +VI and one in +V. Nonetheless, no difference could be observed in the environment of the three metal cations due to the presence of the C_3 axis of symmetry. The remaining electron is therefore likely to be equally shared by the three equivalent cations.[9] After $[U_2(O\mathit{t}Bu)_9]$ (+IV and +V) and $[\{(THF)U(OPh)_3(\mu_2\text{-}OPh)(\mu_3\text{-}O)(UO_2)(THF)\}_2]$ (+V and +VI), **1** is only the third mixed-valence uranium alkoxide to be described.[8][6b] Each metal cation is coordinated by seven donor atoms: The geometry around the uranium center is a distorted capped trigonal prism [O(1)−O(3)−O(2) and O(5)−Cl(1)−O(2B) define the faces of the prism, while O(4) is the cap]. The "$U_3Cl_3(\mu_3\text{-}O)(\mu_2\text{-}OR)_3$" core results from the arrangement of three such polyhedrons sharing an edge [O(5)−O(2) and its symmetry equivalents]. One molecule of pyridine is present in each calix[4]arene cavity. Whereas fused "double calixarenes" are well-known species in coordination chemistry and have been successfully used in the synthesis of metal networks,[10] **1** is the first example of a fused "triple calixarene" (Figure 2).[11] Complex **1** organizes three cone-shaped cavities and directs them in three directions of space that are separated by an angle of 120°. These three macrocycles are occupied by guest pyridine molecules in the solid state. If an adequate inclusion spacer was found to link these cavities, **1** could represent a unique paramagnetic building block for the design of new supramolecular two-dimensional networks. The other potential interest of **1** is the study of the reactivity that could take place around the remaining chloride anions. The example of $[cis\text{-}Cl_2W(L[4])]$ has already proven that a rich chemistry could be built around the displacement of the halide ligands of a metal calixarene complex.[12]

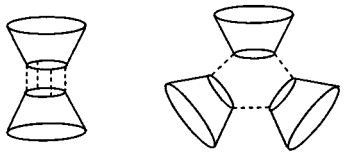

Figure 2. Schematic representation of the fused "double" and "triple" calixarenes

Complex **2** is a dinuclear complex located around a μ_2-oxo bridge (Figure 3). The two-electron donor, O(6), sits on the inversion center of the molecule and binds the two metal cations in a perfectly linear fashion. The U−O−U moiety is then sandwiched between two fully deprotonated *t*Bu-calix[5]arene units. Such a linear mode of binding [U(1)−O(6) 2.0969(9) Å] is commonplace in uranium chem-

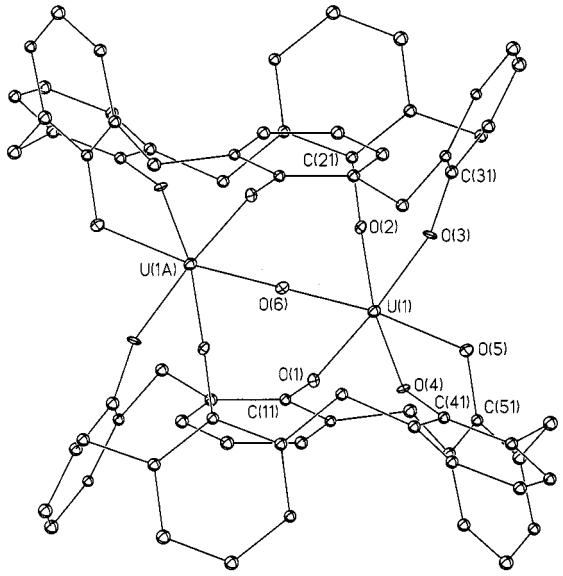

Figure 3. X-ray structure of complex **2**; all *t*Bu groups, hydrogen atoms, and solvent molecules have been omitted for clarity; respective selected bond lengths and mean bond lengths [Å] and angles [°] with estimated standard deviations in parentheses for **2** and **3**: U(1)−O(1) 2.141(9), 2.159(6); U(1)−O(2) 2.158(9), 2.112(6); U(1)−O(3) 2.110(9), 2.112(6); U(1)−O(4) 2.155(9), 2.154(6); U(1)−O(5) 2.186(9), 2.143(6); U(1)−O(6) 2.0969(9), 2.078(6); U(1)−O(1)−C(11) 152.0(8), 153.0(6); U(1)−O(2)−C(21) 142.4(8), 149.1(6); U(1)−O(3)−C(31) 160.8(8), 155.6(6); U(1)−O(4)−C(41) 156.0(7), 154.4(6); U(1)−O(5)−C(51) 120.9(7), 123.6(5)

istry.[13] The geometry around the metal center is distorted octahedral [minimum and maximum O−U−O angles equal 83.0(4) and 96.3(4)°, respectively] with each $L[5]^{5-}$ ligand binding the first uranium cation with three of its phenolate groups and the second metal cation with the other two. Of the 6 pyridine molecules found in the lattice, four were found to form pyridinium dimers (N−HN bond length of 2.98 Å). One of the pyridine molecules of the dimer is included in the cavity of the macrocycle. Such inclusion of a cation in the aromatic cavity of a calixarene is a common feature in calixarene chemistry.[14] The presence of two organic cations in the lattice implies that **2** is in fact a dianionic complex of U(+V). The broad paramagnetic signals observed in the NMR spectrum and the typical dark-red color further confirm the valency deduced from the X-ray analysis. Whereas numerous examples of U^V homoleptic alkoxides are reported in the literature,[15] it seems that mixed oxo-alkoxides such as **2** have not yet been described for this particular oxidation state. If molecules of the type $[OU(OR)_3]$ have been mentioned briefly by Bradley, they have not been well characterized by today's standards.[16] Complex **2** is also a unique example of a "double calixarene" made by the fusion of two cone-shaped calix[5]arenes. While such species are well known for the calix[4]arenes, they are more unusual for the larger macrocycles. To the best of our knowledge, the uranyl dimer $[\{UO_2(H_2L[6])\}_2]$ is the only other such compound present in the literature.[17] The closest related compound is $[Eu_2(H_2L[5])_2(dmso)_4]$, a bimetallic lanthanide complex held together by two *t*Bu-calix[5]arenes, but where the macrocycle is not in the cone conformation.[18]

As a powder or as a solution, **1** slowly decomposes to insoluble products when exposed to air. Conversely, a solution of **2** in a mixture of pyridine and acetone immediately oxidizes and turns to a light red. This solution slowly deposits beautiful single crystals among other uncharacterized decomposition products. The crystal structure was solved and revealed $[\{U(L[5])\}_2O]$ (**3**), the U^{VI} homologue of **2**.

$$[HNC_5H_5]_2[\{U(L[5])\}_2O] \xrightarrow[O_2]{\text{pyridine}} [\{U(L[5])\}_2O] + \text{decomposition products}$$

The geometry of **3** is similar to that of **2**, and no shortening of the U−O distances is observed, however the oxidation state is unambiguously confirmed by the diamagnetic NMR spectrum and by the lighter color of the complex. A pyridine molecule occupies the cavity of the calixarene in the solid state. Complex **3** is stable when exposed to air as a solid powder but slowly decomposes in the various solvents we used. The possibility of oxidizing U^V alkoxides into their U^{VI} derivatives by means of alcoholysis has been known for a long time, however the latter are strong oxidizing species that can also be used as intermediates in the synthesis of lower oxidation state complexes.[19] The oxidation of **2** to **3** does not lead to changes in the coordination geometry of the metal center and is a good example of the robustness conferred to the complex by the bridging macrocycle.

While the reactions of $H_4L[4]$ and $H_5L[5]$ with UCl_4 bear some resemblance in the kinds of oxo compounds they deliver, the reaction of $H_6L[6]$ does not follow the same pathway. When UCl_4 is treated with $H_6L[6]$ in pyridine, the pale green solution never turns to red. After hours of heating a mixture of the two reagents in pyridine under reflux, a change of color was eventually observed. Although the NMR spectrum of the mixture indicates that a reaction had possibly taken place,[20] we never managed to isolate a complex at this stage of the procedure. However, when the reaction mixture was exposed to air, the brown-green color immediately turned to a bright red. The solution was allowed to stand and after a few days, crystals suitable for X-ray crystallography were isolated. The structure was solved and revealed that $[U(H_3L[6])_2]$ (**4**) had been formed among other uncharacterized decomposition products.

$$UCl_4 + 2\,H_6L[6] \xrightarrow[O_2]{\text{pyridine}} [U(H_3L[6])_2] + \text{decomposition products}$$

Complex **4** is a U(+VI) complex, where two $H_3L[6]$ ligands coordinate the metal cation through three successive phenolate groups (Figure 4). The metal cation is the center of inversion of the complex. Its coordination geometry is thus a distorted octahedron [minimum and maximum O−U−O angles equal 85.6(3) and 94.4(3)°, respectively] with classical U−O bond lengths. Complex **4** can be viewed as an homoleptic uranium alkoxide. These are known since the early days of the Manhattan project, which started 5f-metal coordination chemistry.[21] However, only a few of

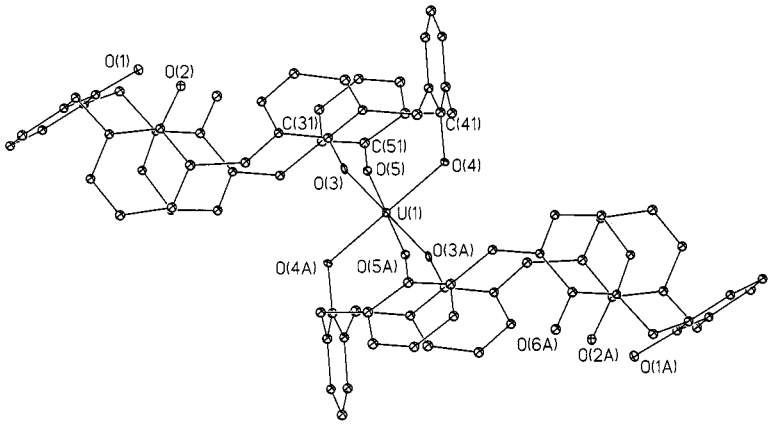

Figure 4. X-ray structure of complex **4**; all *t*Bu groups, hydrogen atoms, and solvent molecules have been omitted for clarity; selected bond length [Å] and angles [°] with estimated standard deviations in parentheses: U(1)−O(3) 2.10(1), U(1)−O(4) 2.132(8), U(1)−O(5) 2.112(9); U(1)−O(3)−C(31) 164.3(7), U(1)−O(4)−C(41) 126.(8), U(1)−O(5)−C(51) 169.1(8)

these compounds have been characterized by means of X-ray diffraction,[8,15a,15c,22] and none of them is a U^{VI} complex.[23] Complex **4** is the first "$U(OR)_6$" complex to be characterized by single-crystal X-ray diffraction. Its coordination geometry is close to the octahedral one of [$U(OTeF_5)_6$].[24] The conformation of the calixarene is 1,2,3-alternate, with the aromatic faces bearing the phenolic groups defining the first partial cone, and the three corresponding to the phenolate groups defining the second. This conformation is commonplace for the uncoordinated calix[6]arene derivatives, but had, to the best of our knowledge, never been encountered among the crystal structures of their metal complexes.[25] The fusion of two 1,2,3-alternate calix[6]arene affords a molecule with four aromatic cavities (Figure 5). In the solid state, all these half-cones are filled by pyridine molecules, thus **4** is the host to four molecular guests.

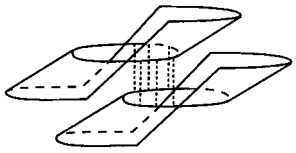

Figure 5. Schematic representation of **4** emphasizing its four half-cone cavities

In conclusion, the reactions of UCl_4 with $H_4L[4]$, $H_5L[5]$, and $H_6L[6]$ enabled us to synthesize **1**, **2**, and **4**, the three first "non-uranyl" calixarene complexes of uranium. Complex **2** oxidizes to yield its U^{VI} equivalent **3** when exposed to air. The oxidation state of the metal ion in **1**−**4** is +V or +VI. If **1**−**3** contain μ-oxo bridges, **4** can be seen as a homoleptic uranium alkoxide. The isolation of **1**−**4** represents an exceptional example of the diversity of uranium compounds, and of the various molecular architectures that can be obtained from ring-size variation of a large polyalkoxide ligand. This reinforces the idea that a rich chemistry can be built at the boundary between macrocycle, supramolecular, and coordination chemistries.

Experimental Section

All NMR spectra were performed with a Bruker DPX-200. − Elemental analyses were performed at Analytische Laboratorien, D-51789 Lindlar, Germany. − Unless specified, all reactions were performed in a glove box under dry N_2. $H_4L[4]$, $H_5L[5]$, and $H_6L[6]$ were dried under vacuum for 12 h at 323 K prior to use. Pyridine was dried with K (***Caution!***) and distilled prior use.

Synthesis of 1: UCl_4 (0.050 g, 0.130 mmol) was treated with $H_4L[4]$ (0.085 g, 0.130 mmol) in pyridine (20 mL) at 333 K for 12 h. The black solution obtained was filtered and concentrated under vacuum (10 mL). It was then left standing overnight to afford a black microcrystalline powder that was filtered off, washed with cold pyridine and dried in vacuo to afford $[\{UCl(L[4])\}_3O] \cdot 2\,(NC_5H_5)$ (0.018 g, 0.006 mmol, 14%). − ^{1}H NMR: δ = 20.12, 16.08, 11.36, 11.11, 9.60, 9.21, 9.00, 6.20, 5.63, 3.59, 3.38, 1.91, 1.87, 1.77, 1.68, 1.65, 1.61, 1.58, 1.55, 1.48, 1.23, 1.09, −0.13, −0.21, −0.34, −4.00, −14.23.[9] − $C_{142}H_{166}Cl_3N_2O_{13}U_3$ (2927.9): calcd. C 58.25, H 5.67, N 0.96; found C 58.03, H 5.75, N 0.93.

Synthesis of 2: UCl_4 (0.050 g, 0.130 mmol) was treated with $H_5L[5]$ (0.107 g, 0.130 mmol) in pyridine (20 mL) at 333 K for 12 h. The dark red solution obtained was filtered and concentrated under vacuum (10 mL). It was then left standing overnight to afford a red microcrystalline powder that was filtered off. This powder was slowly recrystallized in pyridine to afford $[HNC_5H_5]_2$-$[\{U(L[5])_2O] \cdot 4\,(NC_5H_5)$ as beautiful single crystals (0.029 g, 0.011 mmol, 17%). − ^{1}H NMR: δ = 14.04 (br., 8 H, ArH), 8.81 (br., 4 H, ArH), 7.95 (br., 8 H, ArH), 6.39 (br., 8 H, Ar−CH_2−Ar), 4.68 (br., 8 H, Ar−CH_2−Ar), 1.63 (36 H, *t*Bu), 1.34 (18 H, *t*Bu), 0.97 (36 H, *t*Bu), −1.22 (br., 4 H, Ar−CH_2−Ar). − $C_{140}H_{162}N_6O_{11}U_2$ (2579.5): calcd. C 65.18, H 6.28, N 3.26; found C 65.24, H 6.49, N 3.33.

Synthesis of 3: Compound **2** (0.020 g, 0.008 mmol) was dissolved in a 50% mixture of pyridine and acetone (2 mL) at room temperature, and briefly exposed to air. The light-red solution thus obtained was left standing overnight to afford a red microcrystalline powder that was filtered off. This powder was slowly recrystallized in pyridine to afford a mixture of $[\{U(L[5])_2O] \cdot 2.5\,(NC_5H_5)$ as small monocrystals (0.007 g, 0.003 mmol, 37%) and microcrystalline $H_5L[5]$. Successive recrystallization in various solvents did not afford **3** in its elementally pure form. − ^{1}H NMR: δ = 9.11, 8.60,

8.23, 6.99, 6.74 (5 × 4 H, ArH), 6.61, 4.70 (br., 2 × 8 H, Ar−CH_2−Ar), 4.10 (br., 4 H, Ar−CH_2−Ar), 1.62 (36 H, *t*Bu), 1.26 (18 H, *t*Bu), 0.95 (36 H, *t*Bu).

Synthesis of 4: UCl_4 (0.050 g, 0.130 mmol) was treated with $H_6L[6]$ (0.256 g, 0.260 mmol) in pyridine (10 mL) at room temperature for 10 min and then briefly exposed to air. The red solution thus obtained was concentrated under vacuo (2 mL) and left standing for two weeks to deposit a red microcrystalline powder that was filtered off, washed with pentane, and dried in vacuo to afford $[U(H_3L[6])] \cdot 2\,(NC_5H_5)$ (0.030 g, 0.013 mmol, 10%). − 1H NMR: δ = 12.00 (br., 6 H, OH), 8.59, 8.45, 8.24, 7.72, 7.22, 6.88 (6 × 4 H, ArH), 6.73, 5.93, 4.31 (br., 3 × 8 H, Ar−CH_2−Ar), 1.55 (36 H, *t*Bu), 1.46 (18 H, *t*Bu), 1.17 (18 H, *t*Bu), 0.80 (36 H, *t*Bu). − $C_{142}H_{172}N_2O_{12}U$ (2335.4): calcd. C 73.02, H 7.36, N 1.20; found C 72.70, H 7.61, N 0.98.

X-ray Crystallographic Studies: Crystal data collection was performed with a Nonius Kappa CCD diffractometer equipped with a fiber glass collimator. Copies of the crystallographic data of **1**, **2**, **3**, and **4** can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44 1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal Data of $1 \cdot 11.5\,(NC_5H_5)$: $C_{189.5}H_{213.5}N_{11.5}Cl_3O_{13}U_3$ (3680.7), 0.24 × 0.20 × 0.18 mm, trigonal, *P*−3*c*1, *Z* = 4, *a* = 21.576(3), *b* = 21.576(3), *c* = 45.517(9) Å, α = 90, β = 90, γ = 120°, *V* = 18350(5) Å^3, $\rho_{calcd.}$ = 1.333 g·cm^{-3}, *F*(000) = 7460, $2\theta_{max}$ = 60.58°, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), μ_{Mo} = 2.744 cm^{-1}, *T* = 123 K. The structure was solved by direct methods,[26] and refined on F^2.[27] Of the 26624 reflections measured, 8902 were found to be independent (R_{int} = 0.123), 4419 of which were considered as observed [$I > 2\sigma(I)$] and were used in the refinement of the 427 parameters, leading to a final R_1 of 0.0844 and a R_{all} of 0.1942. wR_{obs} and wR_2 were found to be 0.1681 and 0.2369, respectively. Hydrogen atoms were introduced in the calculation as riding on calculated positions. The goodness-of-fit parameter *S* was 1.134 and the maximum residual density 0.960 eÅ^{-3}. Crystallographic data (excluding the structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140041.

Crystal Data of $[HNC_5H_5]_2[2] \cdot 4\,(NC_5H_5)$: $C_{140}H_{162}N_6O_{11}U_2$ (2580.8), 0.24 × 0.18 × 0.18 mm, monoclinic, *P*2(1)/*n*, *Z* = 2, *a* = 12.580(3), *b* = 19.950(4), *c* = 25.120(5) Å, α = 90, β = 98.74(3), γ = 90°, *V* = 6231(2) Å^3, $\rho_{calcd.}$ = 1.376 g·cm^{-3}, *F*(000) = 2632, $2\theta_{max}$ = 41.48°, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), μ_{Mo} = 2.657 cm^{-1}, *T* = 123 K. The structure was solved by direct methods,[26] and refined on F^2.[27] Of the 35322 reflections measured, 6267 were found to be independent (R_{int} = 0.094), 3006 of which were considered as observed [$I > 2\sigma(I)$] and were used in the refinement of the 280 parameters, leading to a final R_1 of 0.0659 and a R_{all} of 0.1739. wR_{obs} and wR_2 were found to be 0.1110 and 0.1506, respectively. Solvent pyridine molecules were constrained to regular hexagons. Uranium and oxygen atoms were considered anisotropic. All the other atoms were considered as isotropic in order to keep a reasonable data/parameters ratio. Hydrogen atoms were introduced in the calculation as riding on calculated positions. The goodness-of-fit parameter *S* was 0.995 and the maximum residual density 0.705 eÅ^{-3}. Crystallographic data (excluding the structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140042.

Crystal Data of $[3]_2 \cdot 5\,(NC_5H_5)$: $C_{245}H_{285}N_5O_{22}U_4$ (4603.9), 0.18 × 0.18 × 0.12 mm, monoclinic, *P*2(1)/*n*, *Z* = 4, *a* = 26.907(5), *b* = 28.012(6), *c* = 31.015(6) Å, α = 90, β = 107.16(3), γ = 90°, *V* = 22336(8) Å^3, $\rho_{calcd.}$ = 1.369 g·cm^{-3}, *F*(000) = 9336, $2\theta_{max}$ = 41.64°, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), μ_{Mo} = 2.955 cm^{-1}, *T* = 123 K. The structure was solved by direct methods[26] and refined on F^2.[27] Of the 171260 reflections measured, 22846 were found to be independent (R_{int} = 0.0682), 15455 of which were considered as observed [$I > 2\sigma(I)$] and were used in the refinement of the 1455 parameters, leading to a final R_1 of 0.0473 and a R_{all} of 0.0889. wR_{obs} and wR_2 were found to be 0.0982 and 0.1158, respectively. Uranium and oxygen atoms were considered anisotropic. All the other atoms were considered as isotropic in order to keep the number of parameters smaller than 1500. Above this value our refinement software is unable to operate. Hydrogen atoms were introduced in the calculation as riding on calculated positions (*U* = 1.2 times that of the corresponding atom). Solvate molecules of pyridine were refined as regular hexagons. The goodness-of-fit parameter *S* was 1.084 and the maximum residual density 1.226 eÅ^{-3}. The latter was located in the center of the thermally agitated solvent molecule bearing N(5). Crystallographic data (excluding the structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140040.

Crystal Data of $4 \cdot [HNC_5H_5]_2Cl_2 \cdot 10\,(NC_5H_5)$: $C_{192}H_{224}Cl_2N_{12}O_{12}U$ (3200.7), 0.18 × 0.12 × 0.12 mm, triclinic, *P*−1, *Z* = 1, *a* = 15.770(3), *b* = 16.680(3), *c* = 17.380(4) Å, α = 84.24(3), β = 72.78(3), γ = 87.35(3)°, *V* = 4344(2) Å^3, $\rho_{calcd.}$ = 1.224 g·cm^{-3}, *F*(000) = 1682, $2\theta_{max}$ = 41.90°, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), μ_{Mo} = 1.027 cm^{-1}, *T* = 123 K. The structure was solved by direct methods,[26] and refined on F^2.[27] Of the 14651 reflections measured, 8598 were found to be independent (R_{int} = 0.156), 4672 of which were considered as observed [$I > 2\sigma(I)$] and were used in the refinement of the 482 parameters, leading to a final R_1 of 0.0918 and a R_{all} of 0.1829. wR_{obs} and wR_2 were found to be 0.1984 and 0.2613, respectively. Solvent pyridine molecules were constrained to regular hexagons. Uranium, chlorine, and oxygen atoms were considered anisotropic, as well as the carbon atoms of the non-disordered methyl of the *t*Bu groups. All the other atoms were considered as isotropic in order to keep a reasonable data/parameters ratio. Hydrogen atoms were introduced in the calculation as riding on calculated positions. The goodness-of-fit parameter *S* was 1.095 and the maximum residual density 0.848 eÅ^{-3}. Crystallographic data (excluding the structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140043.

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Received February 10, 2000
[I00044]