Caesium Control of the Coordination Chemistry of *t*Bu-calix[6]arene towards Uranyl

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Received June 3, 1998

Keywords: Calixarenes / Uranyl / Caesium / Supramolecular chemistry

The reaction of $[UO_2Cl_4]^{2-}$ with *t*Bu-calix[6]arene (H_6L) is made possible by the presence of Cs^+ leading to the formation of a trimetallic inclusion complex. An alkali metal can definitely influence the coordination chemistry of *t*Bu-calix[6]arene.

Calixarenes as ligands is a fast developing field of supramolecular chemistry. However, it almost exclusively concerns calix[4]arene derivatives.[1] Amongst all metal complexes currently studied, those of the lanthanides[2] and actinides[3] are receiving particular attention due to environmental needs.[4] Although calix[6]arene derivatives were soon recognised as matching the coordination geometry required by the uranyl ion,[5] it has not been possible to isolate the simple inclusion complex with UO_2^{2+}. Structural information on how this family of ligands binds to metals are still scarce[6][3d]. Recently, Gibson suggested that “alkali-metal ions could influence the coordination and reactivity of calix[4]arene at transition metal centres”.[7] In order to test this idea for larger calixarenes, we decided to study the possible effect of an alkali metal on the reactivity of *t*Bu-calix[6]arene (H_6L) towards uranyl. We report here the dramatic influence of Cs^+ on the reaction of H_6L with $[UO_2Cl_4]^{2-}$ and the synthesis, X-ray determination, and NMR study of the new caesium inclusion complex $[Cs][HNC_5H_5]_3[UO_2Cl_2]_2[H_2L]\cdot 7\ NC_5H_5$ (**1**).

When $[HNC_5H_5]_2[UO_2Cl_4]$[8] was treated with H_6L in pyridine, no reaction was observed. Even after refluxing the two components for 12 hours, the ^1H NMR of the calixarene and the visible spectrum of the uranyl cation were identical to the ones of the starting materials.

Scheme 1

$$2\,[HNC_5H_5]_2[UO_2Cl_4] + H_6L \xrightarrow[\text{pyridine}]{} \text{no reaction}$$

However, when one equivalent of caesium triflate was added to the mixture, the pale yellow colour immediately turned to a deep red.

Scheme 2

$$2\,[HNC_5H_5]_2[UO_2Cl_4] + H_6L \xrightarrow[\text{pyridine}]{Cs^+} [Cs][HNC_5H_5]_3[UO_2Cl_2]_2[H_2L] + 4\,[HNC_5H_5]Cl$$

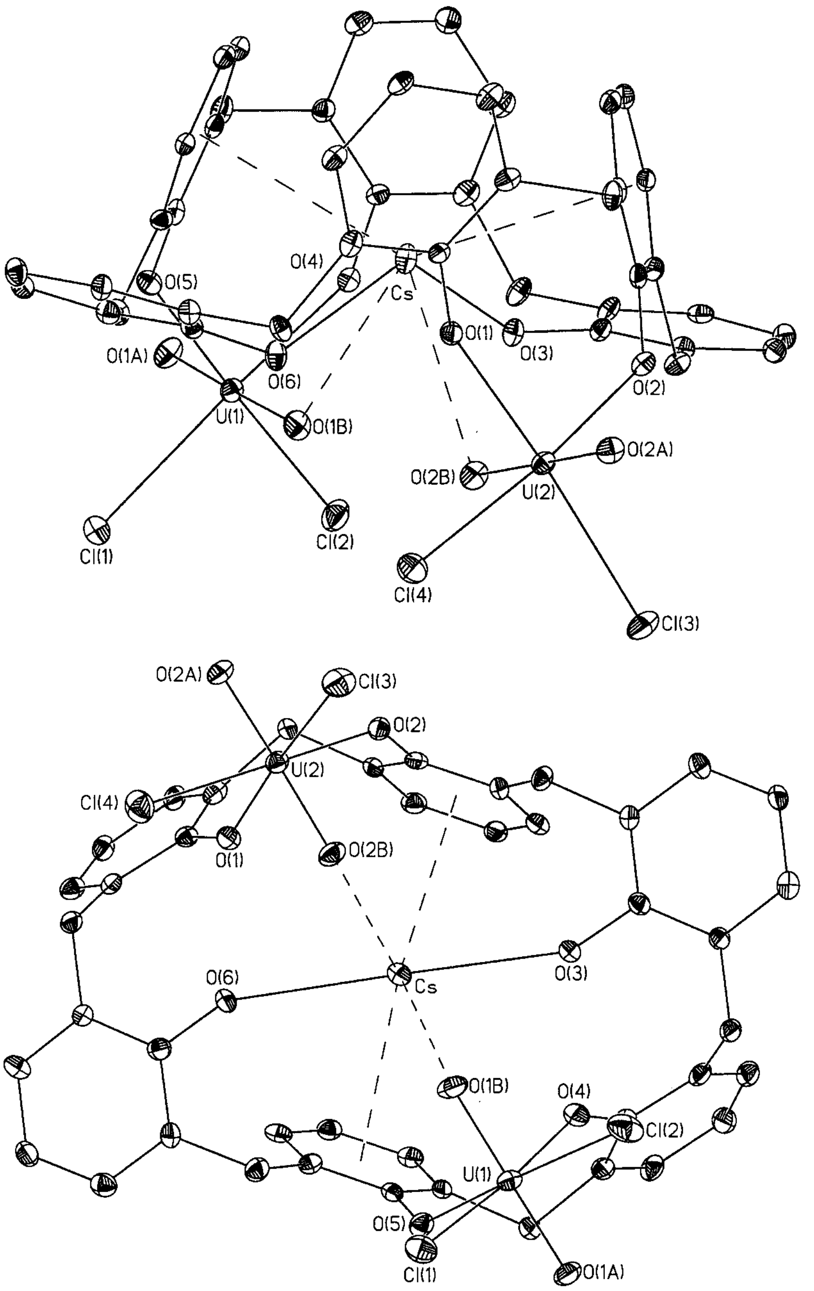
The solution was allowed to stand and after two days red crystals of **1** suitable for X-ray crystallography (59% yield) were isolated as the sole reaction product. The structure was solved and revealed an heterotrimetallic complex of *t*Bu-calix[6]arene where two uranyl cations and a caesium atom were coordinated to the macrocycle (Figure 1).

Of the ten pyridine molecules found in the lattice, six were found to form three pyridinium dimers (N−H···N bond distance of 2.66 Å), implying that the macrocycle was deprotonated four times to result in the observed stoichiometry for **1**: $[Cs][HNC_5H_5]_3[UO_2Cl_2]_2[H_2L]\cdot 7\ NC_5H_5$.

The two uranyl cations are bound in an external fashion to the macrocycle through the deprotonated oxygen of the phenolate groups. Mean U=O, U−O, and U−Cl bond distances are 1.789(7), 2.214(8), and 2.711(4) Å, respectively, and are comparable with those of the literature.[3b][3c][3d][3e][3f][5c][9] The geometry around uranyl is four-coordinate equatorial with the two phenolate oxygen atoms and the two chloride atoms in *cis* arrangements. This arrangement is unprecedented for an anionic moiety of uranyl ($[UO_2X_2Y_2]^{2-}$) and the only related example found in the literature is the *cis* arrangement of two phosphane oxides and two chlorides in $[UO_2Cl_2(OPPh_3)_2]$.[9]

The caesium cation is bound to the two protonated oxygens of the calixarene that do not form bonds with uranium [O(6) and O(3)]. The mean Cs−O distance is 3.045(8) Å, in agreement with the one found for coordinate bonds in crown ether (3.0−3.3 Å)[10] or in complexes where coordination of an alcohol group to caesium was observed [3.006(6)−3.323(7) Å][11]. More unusual are the short contacts of 3.390(9) and 3.454(8) Å found between the caesium and the two uranyl oxygen atoms [O(1B) and O(2B)]. Although they can not formally be considered as bonds, those interactions probably help to stabilise the caesium inside its host. The alkali cation is also bound in nearly a η^6-fashion to the faces of the two phenolic rings. Cs−C distances range between 3.41(1) and 3.87(1) Å, and the three shortest distances correspond to the phenol- and methylene-substituted

Figure 1. X-ray structure of compound **1** [a] A: side view, B: bottom view. *t*Bu groups have been omitted for clarity



[a] Selected bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: U(1)−O(1A) 1.788(7), U(1)−O(1B) 1.788(7), U(1)−O(4) 2.235(8), U(1)−O(5) 2.196(8), U(1)−Cl(1) 2.723(4), U(1)−Cl(2) 2.708(4), U(2)−O(2A) 1.791(7), U(2)−O(2B) 1.792(7), U(2)−O(1) 2.228(7), U(2)−O(2) 2.197(7), U(2)−Cl(3) 2.694(3), U(2)−Cl(4) 2.718(4), Cs−O(1B) 3.389(8), Cs−O(2B) 3.454(8), Cs−O(3) 3.021(7), Cs−O(6) 3.067(8), O(4)−U(1)−O(5) 87.7(3), O(4)−U(1)−Cl(2) 90.0(2), O(5)−U(1)−Cl(1) 92.5(2), Cl(1)−U(1)−Cl(2) 89.9(1), O(1)−U(2)−O(2) 86.2(3), O(1)−U(2)−Cl(4) 87.9(2), O(2)−U(2)−Cl(3) 95.2(2), Cl(3)−U(2)−Cl(4) 90.9(1), O(3)−Cs−O(6) 133.5(2).

positions. The mean Cs−centroid distance is 3.35(1) Å. The shortest Cs−C separations are shorter than those found for caesium−methyl (3.53 Å),[12] and for caesium complexes of *t*Bu-calix[4]arene and bis(homooxa)-*t*Bu-calix[4]arene [3.53(1) to 4.17(1) Å, with a Cs−centroid distance of 3.57(1) Å].[13] They are more in the range of those found for selective caesium extractants like 1,3-calix[4]arene crowns [3.273(5)−3.770(5) Å] although in the latter, the alkali cation is only bound in η^2 or η^3 fashion to the phenolic faces.[14] The short Cs−O and Cs−C distances in **1** imply that caesium is strongly bound within the macrocycle, which, in the case of a ligand as flexible as *t*Bu-calix[6]arene,[15] seems to indicate that the alkali cation guest is not held within the cavity by the suitable size of the host as noticed for the calix[4]arene analogues,[13a][16] but participates in holding together the ligand conformation. The crystal structure of **1** is not only a rare example of a metal complex of an underivatized calix[6]arene,[6a][6c][6e][3d] but is also the first crystallographic example of cationic π-bonding to the inner faces of the phenolic rings of anything other than a calix[4]arene derivative.

The organic macrocycle adopts a pinched-cone conformation reminiscent of that found in the other complex of H_6L and uranyl present in the literature,[3d] but is more distorted. In compound **1**, the angle formed by the two planes of the phenolic rings bound to caesium by their oxygen atoms [O(3) and O(6)] is 18(1)°, and the one formed by the two phenolic rings bound in a polyhapto fashion to caesium, and therefore brought towards each other, is 32(2)°, inverted with respect to the cone conformation (relative to 62° and 11° for equivalent positions in reference 3d).

Synthesis of the analytically pure compound on a preparative scale was achieved by treating $[Cs]_2[UO_2Cl_4]$[8] with H_6L in pyridine.

^1H- and ^{133}Cs-NMR spectroscopy was employed to obtain information about the role of caesium in the formation of the complex. One equivalent of caesium triflate was added to a solution of H_6L in pyridine and a significant shift (−23 ppm) for the caesium signal was observed, as well as the enlargement and shift of the signals of the acidic protons [+0.57 ppm, Full Width at Half Maximum (FWHM) +53 Hz] and methylenic protons (−0.02 ppm, FWHM +7 Hz), demonstrating the modification of the geometry of the calixarene and the formation of a complex with the alkali metal. Although from these NMR data, it is not possible to draw conclusions about the resulting shape of the macrocycle, or the kind of bonding involved, it is possible to imagine that the formation of such Cs−*t*Bu-calix[6]arene species could then enable the reaction with uranyl.

Scheme 3

$$2\,[UO_2Cl_4]^{2-} + [H_6L] + Cs^+ \rightarrow {}'[Cs{-}H_6L]' \rightarrow [Cs][UO_2Cl_2]_2[H_2L]^{\,3-}$$

Unlike the reaction with calix[4]arene complexes of Nb and Ta where metallation of the ligand has been used to bind alkali metal cations in the cavity,[17] the reaction with the alkali metal occurs prior to reaction with uranium in the formation of **1**.

Contrary to observations for the free ligand, the ^1H-NMR spectrum of **1** is characteristic of the restricted motion of the macrocycle, with methylene, *tert*-butyl, and phenyl protons split into several resonances. ^{133}Cs-NMR spectrum of **1** exhibits three peaks, none of them corresponding to the signal of free Cs^+ as obtained for caesium triflate, thus demonstrating that encapsulation of the alkali metal is retained in solution. The three peaks proved to be in slow exchange, but no coalescence could be obtained by temperature change (276 to 346 K) or by addition of excess caesium triflate (up to one equivalent). We assume that this set of peaks could be due to different positions of the caesium atom inside its host, as observed for the calix[4]arene derivatives.[13b]

In conclusion, we have found that the reaction of *t*Bu-calix[6]arene with $UO_2Cl_4{}^{2-}$ could be activated by the presence of caesium. We have characterised a heterotrimetallic complex displaying external coordination of uranyl and inclusion of caesium. The evidence of an initial interaction between the calixarene and Cs^+ demonstrates the influence of the alkali metal on the coordination chemistry reaction. Studies are currently in progress to determine the exact nature of the interaction of caesium and *t*Bu-calix[6]arene in pyridine, and to extend this research to other calixarenes and to other alkali metals.

Experimental Section

General: All experiments were carried out with exclusion of air and moisture in a glove box. ^1H- and ^{133}Cs-NMR spectra were recorded in $[D_5]$pyridine on a Bruker DRX-500 spectrometer at $T = 297$ K. All NMR tubes were charged to obtain a Cs^+ concentration of approximately 2 mmol/l. The 65.6 MHz ^{133}Cs-NMR spectra were calibrated externally relatively to a 0.5 mol/l D_2O solution of CsBr. − Elemental analyses were performed at Service de Microanalyse, CNRS, 91191 Gif-sur-Yvette.

$[Cs][HNC_5H_5]_3[UO_2Cl_2]_2[H_2L]$ (**1**): $[Cs]_2[UO_2Cl_4]$ (CAS no. 17631-98-0) (0.28 g, $4\cdot10^{-4}$ mol) was treated with H_6L (0.20 g, $2\cdot10^{-4}$ mol) in pyridine (30 ml) at 323 K for 12 hours. After filtration of a white powder of CsCl, the solution was concentrated and compound **1** was obtained as a red powder. After recrystallisation in pyridine, the powder was dried under vacuum and gave satisfactory elemental analysis for $[Cs][HNC_5H_5]_3[UO_2Cl_2]_2[H_2L]$ (0.27 g, $1.3\cdot10^{-4}$ mol, 65%). − ^1H NMR $\delta = 1.34$ (m, 18 H, *t*Bu), 1.21 (m, 36 H, *t*Bu), 3.39, 3.82, 4.00, 4.11, 5.31, 6.16, 6.54 (br s, 12 H, $ArCH_2Ar$), 6.86, 7.24, 7.30, 7.41, 7.78 (12 H, ArH), 9.86, 12.75 (5 H, H^+): − ^{133}Cs NMR $\delta = 23$ (br s, 20 Cs), −78(br s, 10 Cs), −128 (br s, 24 Cs). − $C_{81}H_{98}Cl_4CsN_3O_{10}U_2$ (2023): calcd. C 48.05, H 4.84, N 2.08; found C 47.98, H 5.09, 2.41.

Reaction of H_6L with Caesium Triflate: An NMR tube was charged with H_6L (10 mg, $1\cdot10^{-2}$ mmol) in $[D_5]$pyridine (0.4 ml) and caesium triflate (3 mg, $1\cdot10^{-2}$ mmol) was added. − ^1H NMR $\delta = 1.21$ (s, 54 H, *t*Bu), 4.10 (s, 12 H, $ArCH_2Ar$, FWHM = 15 Hz), 7.31 (s, 12 H, ArH), 11.37 (br s, 6 H, H^+, FWHM = 97 Hz), − ^{133}Cs NMR $\delta = -5$(br).

Reference ^1H NMR Spectrum of H_6L: $\delta = 1.21$ (s, 54 H, *t*Bu), 4.12 (s, 12 H, $ArCH_2Ar$, FWHM = 8 Hz), 7.29 (s, 12 H, ArH), 10.80 (br s, 6 H, H^+, FWHM = 44 Hz).

Reference ^{133}Cs NMR spectrum of Caesium Triflate: $\delta = 18$(s).

X-ray Crystallographic Study: Crystal data of **1**; $C_{116}H_{133}Cl_4CsN_{10}O_{10}U_2$ (2578.09), $0.75 \times 0.55 \times 0.40$ mm^3, triclinic, $P\bar{1}$, $Z = 2$, $a = 15.391(4)$, $b = 17.059(7)$, $c = 24.356(4)$ Å, $\alpha = 83.86(3)$, $\beta = 88.60(2)$, $\gamma = 67.60(4)°$, $V = 5877(3)$ Å^3, $\rho_{calcd} = 1.457$g.cm^{-3}, $F(000) = 2572$, $2\theta_{max} = 24°$, $\mu_{Mo} = 3.206$ cm^{-1}, Enraf-Nonius Mach 3 diffractometer ($\omega/2\theta$ scans, $T = 293$ K, Mo-$K\alpha$ radiation $\lambda = 0.71069$ Å). The structure was solved by the heavy-atom method and refined on F^2 using SHELXTL with all atoms considered as anisotropic except solvated pyridine molecules which were constrained to regular hexagons. One of them was found to be disordered over two positions which could be refined to final occupations 0.89(2) and 0.13(2). Absorption was corrected using ψ-scans (min. transmission = 57.7%, max. transmission = 99.9%). 15765 measured reflections, 11403 of which were considered as observed ($I > 2\sigma I$), 823 refined parameters, $R1 = 0.0608$, $wR2 = 0.1558$ (all data), residual electron density 0.82 eÅ^{-3}. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101252. Copies of the data 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.as.uk].

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[I98173]