Using a large calixarene as a polyalkoxide ligand: *tert*-butylcalix[12]arene and its complex with the uranyl cation

Pascal C. Leverd,*[a] Isabelle Dumazet-Bonnamour,[b] Roger Lamartine[b] and Martine Nierlich[a]

[a] *CEA-Saclay, Service de Chimie Moléculaire, Bât. 125, 91191 Gif sur Yvette, France. E-mail: leverd@drecam.cea.fr*
[b] *Laboratoire de Chimie Industrielle, CNRS-UMR 5078, Université Claude Bernard, 69622 Villeurbanne, France*

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***tert*-Butylcalix[12]arene ($H_{12}L$) encompasses two uranyl bimetallic units inside its cavity to form $[HNEt_3]_2[\{(UO_2)_2(NO_3)(py)\}_2(H_4L)]$ 1, the first metal complex of a large calixarene; the comparison of the crystal structures of 1 and $H_{12}L$ shows a relatively limited influence of metal coordination on the conformation of the macrocycle.**

The coordination chemistry of the calixarenes exclusively concerns calix[4,5,6,7 and 8]arenes and their various derivatives.[1,2] Working with the large calix[$n > 8$]arenes is considered a challenge and very little organic and physical chemistry has been reported for this class of molecules.[3] The calixarene with the highest number of phenolic units for which structural information is currently available is calix[8]arene.[4] The major interest of the calix[$n > 8$]arenes in coordination chemistry is that these large and flexible polyalkoxide ligands have the potential to assemble several metallic units inside their cavity and could lead to new molecular architectures. In an attempt to widen the use of calixarenes in coordination chemistry, we set out to study *tert*-butylcalix[12]arene ($H_{12}L$)[3a,b] as a ligand for the uranyl cation. We report herein, the crystal structure of $H_{12}L\cdot10py$, the first of a large calixarene, and comparison with that of $[HNEt_3]_2[\{(UO_2)_2(NO_3)(py)\}_2(H_4L)]$ **1**, the first metal complex with a ligand of this class. To the best of our knowledge, **1** is a unique example of an organic macrocycle binding two bimetallic species inside its cavity.

Crystals of $H_{12}L$ suitable for X-ray crystallography were obtained from pyridine–acetonitrile (1 : 1) (0.050 g $H_{12}L$ in 10 ml) that was slowly evaporated at 290(1) K over 180 days.†‡ The structure was solved and revealed $H_{12}L\cdot10py$ a pyridine solvate of the fully protonated macrocycle (Fig. 1). In the solid state, $H_{12}L$ is located around a crystallographic centre of inversion. All its phenolic groups engage in strong H-bonding. Four successive intramolecular H-bonds are formed between O(4), O(3), O(2), O(1) and O(6) while O(5) and O(6) bind to pyridine molecules. The all-in conformation of the calixarene is at first reminiscent of that described for *tert*-butylcalix[8]arene.[5] However, a closer look at the dihedral angles between the adjacent phenolic faces indicates that the conformation cannot be described as a pleated loop or a cone.[6,7] In order to define the overall shape of the macrocycle, attention was paid to the relative positions of the phenolic rings [the centroid of the ring bearing O(n) is denoted X(n)]. X(2), X(5) and their two symmetry equivalents define a perfect plane above which are located X(3) and X(4) (+1.37 and +2.50 Å, respectively) and below which are positioned X(1) and X(6) (−4.70 and −3.90 Å, respectively). With this work, $H_{12}L$ becomes the first large calixarene to have its solid state conformation determined by X-ray crystallography.

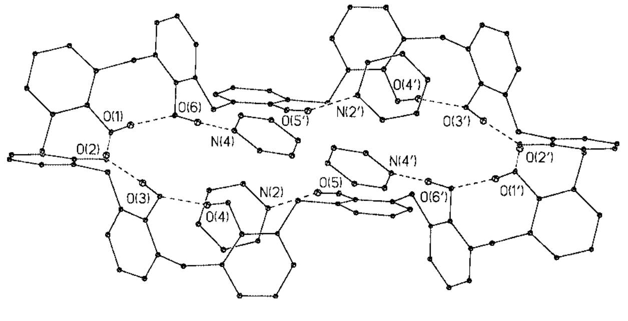

Fig. 1 Crystal structure of compound $H_{12}L$ (5% probability). All Bu^t groups and H atoms or solvent molecules not participating in H-bonding have been omitted for clarity. H-bond donor–acceptor distances (Å): O(1)–O(6) 2.57(3), O(2)–O(1) 2.63(3), O(3)–O(2) 2.61(3), O(4)–O(3) 2.66(3), O(5)–N(2) 2.82(4), O(6)–N(4) 2.56(4).

When $UO_2(NO_3)_2\cdot6H_2O$ was treated with $H_{12}L$ in the presence of NEt_3 in pyridine, a red solution typical of a phenolate complex of uranyl was immediately obtained. The solution was allowed to stand and after a few days a red microcrystalline powder of **1** was obtained as the sole reaction product in 46% yield.†

The synthesis was repeated in a crystallisation vessel (10 mL) which was allowed to stand at 290(1) K. After 180 days, very small crystals suitable for X-ray crystallography were isolated from the same mixture of solvent as for $H_{12}L$.‡ The structure was solved and revealed a complex in which four uranyl cations are encompassed by the macrocyclic ligand (Fig. 2).

As for $H_{12}L$, **1** is located around a centre of symmetry in the solid state. The four uranyl dications form two symmetry related bimetallic units in which the two metal cations are bound by a tridentate nitrate ligand. Such a bis-chelating binding mode of $[NO_3]^-$ is not unusual for solid state polymers, however, it is more rarely found for discrete metal complexes.[8,9] The bimetallic units are bound to the macrocycle through five of its oxygen atoms, four of which are deprotonated [O(1), O(2), O(4) and O(5)]. The resulting short U–O distances (*ca.* 2.2 Å) are typical of uranyl phenolate complexes while the longer U(1)–O(3) distance [2.62(3) Å] corresponds to the dative bond

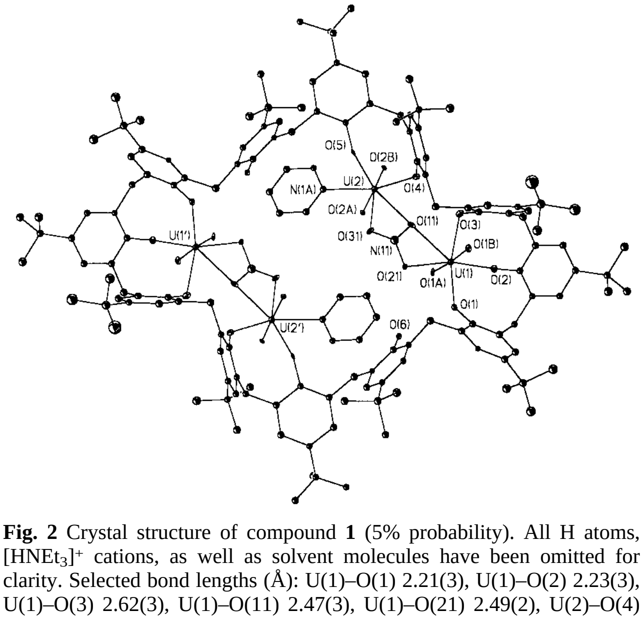

Fig. 2 Crystal structure of compound **1** (5% probability). All H atoms, $[HNEt_3]^+$ cations, as well as solvent molecules have been omitted for clarity. Selected bond lengths (Å): U(1)–O(1) 2.21(3), U(1)–O(2) 2.23(3), U(1)–O(3) 2.62(3), U(1)–O(11) 2.47(3), U(1)–O(21) 2.49(2), U(2)–O(4) 2.32(3), U(2)–O(5) 2.15(3), U(2)–O(11) 2.41(3), U(2)–O(31) 2.46(3), U(2)–N(1A) 2.58(2).

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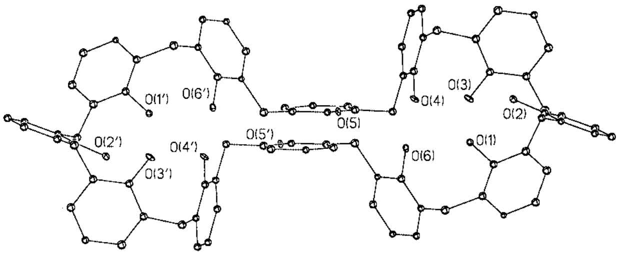

Fig. 3 Side view of the calixarene core in **1**.

formed by a phenolic group.[10] The geometry around the uranyl ion is five-coordinate pentagonal with one of the uranium atoms completing its coordination sphere with the nitrogen atom of a pyridine molecule.

Interestingly, the arrangement of the metallic species in **1** is reminiscent of that reported for the uranyl complex of an acyclic hexaphenol where the six oxygen atoms of the ligand are coordinated to the $[(UO_2)_2(NO_3)]^{3+}$ core.[9] The latter was presented as an open analogue of calix[6]arene but can also be viewed as the half of a calix[12]arene. The macrocyclic geometry of $H_{12}L$ does not enable such flexibility and is probably the cause of the unprecedented arrangement of the donor atoms observed for the metallic species of **1**, in which one of the cations is coordinated by five oxygen atoms and the other by only four, plus a nitrogen atom. To the best of our knowledge, **1** is the first example of an organic macrocycle carrying two bimetallic units inside its cavity. The isolation of **1** reinforces the notion that large polyalkoxide ligands such as calixarenes can be considered as potential ‘cluster-keepers’.[3]

$H_{12}L$ acts as a double pentadentate ligand. As indicated by the stoichiometry and the U–O bond distances, only O(3) and O(6) have been able to retain their acidic proton. The calixarene is thus deprotonated eight times, with the negative charges evenly distributed around the macrocycle.[11] The conformation of the macrocycle is a regular succession of distorted pleated-loops and cones.[12] Although its structure appears different from that of $H_{12}L$, it essentially only differs by the positive sign of the fourth dihedral angle ϕ which is negative for the free macrocycle (−4.8°). Had the latter been positive, the conformation of $H_{12}L$ and **1** would have been similar.[13] This result follows Gutsche’s postulate that flexible calixarenes seek conformations which possess as much cone and/or pleated loop character as their geometry permits.[1]

A good indication of the effect of metal coordination on the ligand is obtained by comparison of some intramolecular distances in $H_{12}L$ and **1**. The longest distance for the oxygen atoms of the phenolic groups in $H_{12}L$ is 17.815 Å between O(1) and O(1′) while the shortest is 4.66 Å between O(5) and O(5′). In **1**, these two distances are 15.68 Å between O(2) and O(2′) and 9.94 Å between O(5) and O(5′). Whereas the free ligand is a thin and elongated molecule, **1** is a shorter and wider compound. The macrocycle is stretched open by metal coordination inside its cavity, but retains its global geometry. The side view of the calixarene core (Fig. 3) emphasises best the shape of the macrocycle in **1** and its resemblance to that of the free ligand.

In conclusion, the encompassing of two metal dimers into one macrocycle has a surprisingly limited influence on the conformation of what was considered a very flexible molecule. The use of a large polyalkoxide ligand leads to a new combination of donor atoms around the uranyl cation and seems highly appropriate for the design of new metal complex architectures. Work is in progress to study other large calixarenes.

Notes and references

† *General*: $H_{12}L$ was prepared by the method described in ref. 3(*a*).

Synthesis of $[HNEt_3]_2[\{(UO_2)_2(NO_3)(py)\}_2(H_4L)]$ **1** : $UO_2(NO_3)_2{\cdot}6H_2O$ (0.052 g, 1.04×10^{-4} mol) was treated with $H_{12}L$ (0.050 g, 2.6×10^{-5} mol) and NEt_3 (0.021 g, 2.08×10^{-4} mol) in pyridine (2.5 mL) at 313 K for 2 h. After allowing the red solution to stand for 7 days at room temperature, a red microcrystalline powder of **1** was separated by decanting, washed twice with acetonitrile (2 mL) and dried for 2 h to afford $[HNEt_3]_2$-$[\{(UO_2)_2(NO_3)(py)\}_2(H_4L)]{\cdot}py$ (0.045 g, 1.2 10^{-5} mol, 46%). $C_{159}H_{207}N_7O_{26}U_4$: Calc. C, 53.28; H, 5.78; N, 2.74. Found: C, 53.36; H, 5.35; N, 2.61%.

‡ *Crystal data*: for $H_{12}L{\cdot}10py$: $C_{182}H_{218}N_{10}O_{12}$, M = 2737.66, 0.12 × 0.03 × 0.03 mm, triclinic, $P\bar{1}$, Z = 1, a = 12.232(2), b = 16.072(3), c = 20.841(4) Å, α = 98.25(3), β = 103.53(3), γ = 91.77(3)°, V = 3933(2) Å^3, D_c = 1.156 g cm^{-3}, $F(000)$ = 1476, $2\theta_{max}$ = 49.34°, μ(Mo-Kα) = 0.072 cm^{-1}, T = 100 K. The structure was solved by direct methods[14] and refined on F^2.[15] Of the 23623 reflections measured, 12327 were found to be independent (R_{int} = 0.247), 3687 of which were considered as observed [$I > 2\sigma(I)$] and were used in the refinement of the 439 parameters, leading to a final R_1 of 0.1212 and a R_{all} of 0.3481. wR_{obs} and wR_2 were 0.2145 and 0.3373, respectively. All hydrogen atoms were introduced in the calculation as riding on calculated positions except those of the phenolic groups which were located on the Fourier map. The goodness-of-fit parameter S was 0.989 and the maximum residual density 0.308 e Å^{-3}.

For **1**·9py: $C_{199}H_{247}N_{15}O_{26}U_4$, M = 4217.22, 0.06 × 0.04 × 0.03 mm, triclinic, $P\bar{1}$, Z = 1, a = 10.099(2), b = 22.133(4), c = 25.109(5) Å, α = 114.39(3), β = 94.07(3), γ= 97.50(3)°, V = 5019(2) Å^3, D_c = 1.395 g cm^{-3}, $F(000)$ = 2120, $2\theta_{max}$ = 41.26°, μ(Mo-Kα) = 3.283 cm^{-1}, T = 100 K. The structure was solved and refined as above. Of the 16796 reflections measured, 9436 were found to be independent (R_{int} = 0.214), 3687 of which were considered as observed [$I > 2\sigma(I)$] and were used in the refinement of the 375 parameters, leading to a final R_1 of 0.1397 and a R_{all} of 0.3007. wR_{obs} and wR_2 were 0.2578 and 0.3604 respectively. Hydrogen atoms were introduced in the calculation as riding on calculated positions. The goodness-of-fit parameter S was 1.228 and the maximum residual density 0.988 e Å^{-3}. CCDC 182/1545. See http://www.rsc.org/suppdata/cc/b0/b000909l/ for crystallographic files in .cif format..

1. C. Wieser, C. B. Dieleman and D. Matt, *Coord. Chem. Rev.*, 1997, **165**, 93; J.-C. Bünzli and J. M. Harrowfield, in *Calixarenes, A Versatile Class of Macrocyclic Compounds*, ed. J. Vicens and V. Böhmer, Kluwer Academic Publishers, Dordrecht, 1991, p. 211.
2. J. M. Harrowfield, *Gazz. Chim. Ital.*, 1997, **127**, 663.
3. (*a*) I. Dumazet, J.-B. Regnouf-de-Vains and R. Lamartine, *Synth. Commun.*, 1997, **27**, 2547; (*b*) D. R. Stewart and C. D. Gutsche, *J. Am. Chem. Soc.*, 1999, **121**, 4136; (*c*) R. Mlika, I. Dumazet, M. Gamoudi, R. Lamartine, H. Ben Ouada, N. Jaffrezic-Renault and G. Guillaud, *Anal. Chim. Acta*, 1997, **354**, 283.
4. Mention of the existence of a uranyl complex of *tert*-butylcalix[9]arene can be found in ref. 2, but the experimental details have remained unpublished.
5. C. D. Gutsche, A. E. Gutsche and A. I. Karaulov, *J. Incl. Phenom.*, 1985, **3**, 447.
6. F. Ugozzoli and G. D. Andreetti, *J. Incl. Phenom.*, 1992, **13**, 337; C. D. Gutsche, in *Calixarenes Revisited*, ed. J. F. Stoddart, Monographs in Supramolecular Chemistry, Royal Society of Chemistry, Cambridge, 1998.
7. Pairs of torsion angles (°) in $H_{12}L$ between the rings bearing O(n) and O(n + 1) starting with n = 1: +86.3 −104.6, −97.6 +85.5, +90.5 −100.2, −4.8 −86.2, +69.6 −0.1, +89.6 −100.6. This succession designates the conformation as C_i [+ −, − +, + −, − −, + −, + −] away from the regular (+ −, − +) or (+ −, + −) sequences respectively expected for the pleated loop and cone conformation.
8. (*a*) T. J. R. Weakley, *Inorg. Chim. Acta*, 1982, **63**, 161; (*b*) C. L. Raston, B. W. Skelton, C. R. Whitaker and A. H. White, *Aust. J. Chem.*, 1989, **42**, 771.
9. P. Thuéry and M. Nierlich, *J. Chem. Soc., Dalton Trans.*, 1997, 1481.
10. P. C. Leverd, P. Berthault, M. Lance and M. Nierlich, *Eur. J. Inorg. Chem.*, 1998, 1859.
11. Succession of the oxygen atoms of the calixarene in **1** stressing the regular distribution of the negative charge: O(1)$^-$, O(2)$^-$, O(3)H, O(4)$^-$, O(5)$^-$, O(6)H, O(1′)$^-$, O(2′)$^-$, O(3′)H, O(4′)$^-$, O(5′)$^-$, O(6′)H.
12. Pairs of torsion angles (°) in **1** between the rings bearing O(n) and O(n + 1) starting with n = 1: +89.0 −79.5, −131.4 +76.6, +92.7 −95.0, −61.2 +103.4, −66.7 +8.1, −92 +70.4. The conformation is designated as C_i [+ −, − +, + −, − +, − +, − +]. The twelve pairs of dihedral angles are ordered into two (+ −, − +) alternate sequences, separated by two (− +, − +) regular sequences.
13. If the fourth dihedral angle ϕ (−4.8°) of the free macrocycle was to be positive,[7] the conformation would be designated as C_i [+ −, −+, + −, + −, + −, + −].
14. G. M. Sheldrick, *SHELXS 86, A Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1990.
15. G. M. Sheldrick, *SHELXS 90, A Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1993.

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