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The first metal complex of an acyclic hexaphenol: structure of the binuclear complex of uranyl ions with an analogue of *p-tert*-butylcalix[6]arene *

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The crystal structure of the bimetallic complex between uranyl ions and the acyclic bis(hydroxymethyl)phenolic oligomer $(HOCH_2)[o\text{-}(p\text{-}Bu^tC_6H_2OH)\text{-}o\text{-}CH_2]_6OH$ (H_8L) has been determined; $[(UO_2)_2(H_2L)(NO_3)][NEt_3H]_3\cdot MeOH$ is the first metal complex of an acyclic analogue of a calixarene structurally characterized.

The chemistry and complexation properties of calixarenes are presently an important domain in supramolecular chemistry.[1] However, few studies have been devoted to the investigation of the acyclic analogues of calixarenes, which are intermediates in the calixarene synthesis process,[1–3] and their crystal structures (a three-dimensional search for polyphenols using the Cambridge Structural Database[4] containing 152 000 entries gave only the structures cited[5–7]). Some solution studies have been reported, showing that the acyclic analogues were not as efficient complexing agents as calixarenes towards alkali-metal picrates, indicating a genuine macrocyclic effect,[8] and conversely, that they could be better 'uranophiles' in experiments including dynamic processes, due to higher kinetic parameters.[9] The complexation of organic molecules by such oligomers has also been investigated.[6,10] The crystal structures of bis-, tris- and tetra-phenolic compounds, showing the existence of intra- and inter-molecular hydrogen bonds,[5–7] as well as some structures of metal complexes of bisphenols[11] have been reported. Structures of metal complexes with higher-order polyphenols (bonded in a calixarene-like fashion, by *o*-methylene bridges) have not been reported. On the other hand, some crystal structures of actinide complexes of calixarenes have been described,[12–16] and the interest of calixarene derivatives as 'uranophiles' in solution is well established.[9] We report in this paper the crystal structure of the first metal complex of an acyclic hexaphenol $[(UO_2)_2(H_2L)(NO_3)][NEt_3H]_3\cdot MeOH$ **1** {where $H_8L = (HOCH_2)[o\text{-}(p\text{-}Bu^tC_6H_2OH)\text{-}o\text{-}CH_2]_6OH$}, a binuclear complex of uranyl ions with an analogue of *p-tert*-butylcalix[6]arene. This result opens new perspectives on polyphenols as metal ligands and better understanding of the importance of the cyclic nature of calixarenes in their metal binding ability. The present study deals only with structural determinations; measurement of complexation constants in solution is necessary to compare further the behaviour of the cyclic and acyclic ligands towards uranyl ions. However, the molecular structure of **1** enables us to stress the potentially interesting metal complexing properties of acyclic analogues of calixarenes.

The bis(hydroxymethyl)hexaphenol $(HOCH_2)[o\text{-}(p\text{-}Bu^tC_6H_2OH)\text{-}o\text{-}CH_2]_6OH$ (H_8L) was not obtained by the step-by-step reaction pathways already described,[3,7,10] but as a side-product during the base-catalysed synthesis of *p-tert*-butylcalix[6]arene.[1] The reaction at room temperature between H_8L (150 mg) and an excess of triethylamine (6 cm^3) in chloroform (20 cm^3), followed by the addition of an excess of uranyl nitrate hexahydrate (120 mg) in acetonitrile (30 cm^3) provided a solid that was filtered and recrystallized in methanol to yield dark red crystals of compound **1** suitable for X-ray crystallography.†

The structure determination gives the overall formula $[(UO_2)_2(H_2L)(NO_3)][NEt_3H]_3\cdot MeOH$ in which $[H_2L]^{6-}$ is a hexaanionic form of H_8L. The asymmetric unit contains one complex molecule, which lacks any symmetry element but, as can be seen in Fig. 1, possesses a pseudo-mirror plane, bisecting the line joining U(1) and U(2) and containing N(1) and O(7). Two UO_2^{2+} ions are encompassed by the ligand, each of them bonded to three phenolic oxygen atoms of $[H_2L]^{6-}$ with different U–O distances, two shorter distances in the range 2.16(2)–2.27(2) [mean value 2.21(5)] Å, and a third larger U–O bond in the range 2.43–2.52 Å. The shorter U–O bonds correspond to the distances found for deprotonated oxygen atoms in calixarene complexes and the longer one to those for protonated ones.[12,14,15] A nitrate ion completes the uranium co-ordination sphere, giving the pentagonal equatorial environment suitable for the uranyl ion. The co-ordination mode of NO_3^- is unusual since it is bidentate for each uranium atom, *i.e.* bis-chelating, the oxygen atom O(7) being co-ordinated to both of them. Asymmetrical bis-chelating nitrate ions are known,[18] but the present case is, to our knowledge, the first genuine example

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* *p-tert*-Butylcalix[6]arene is 4,11,18,25,32,39-hexa-*tert*-butyl[1.$_6$]metacyclophane-7,14,21,28,35,42-hexol.

† Crystal data. $C_{86}H_{134}N_4O_{16}U_2$, $M_r = 1956.10$, crystallizes in the monoclinic space group $C2/c$, $a = 42.433(10)$, $b = 16.658(6)$, $c = 35.080(10)$ Å, $\beta = 126.56(3)°$, $U = 19\,916(25)$ Å^3; $Z = 8$, $D_c = 1.305$ g cm^{-3}, $\mu = 31.33$ cm^{-1}, $F(000) = 7920$. A parallelepipedic single crystal (dimension 0.6 × 0.5 × 0.4 mm) was sealed in a glass capillary. The cell constants were obtained from the least-squares refinement of the setting angles of 25 reflections in the range $8 < \theta < 12°$. The data were collected with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation (0.710 73 Å) in the range $1 < \theta < 20°$, at room temperature, in the ω–θ scan mode. 4656 Reflections with $[I > 3\sigma(I)]$ out of 9275 unique reflections measured, were used after Lorentz-polarization correction. Absorption effects were empirically corrected (ψ scans, $T_{min} = 0.81$, $T_{max} = 1.00$). The intensity decay (2.3% in 88 h) was linearly corrected. Analytical scattering factors for neutral atoms were corrected for f' and f''. The uranium atoms were located from a Patterson map and the remaining atoms from subsequent Fourier-difference maps. Uranium atoms, the co-ordinated oxygen atoms and the terminal carbon atoms of the *tert*-butyl groups were refined anisotropically. The terminal oxygen atoms of the linear oligomer, the triethylammonium ions and the methanol molecule have been found but, being affected by high thermal motion, they were not stable during the refinement and were fixed. Hydrogen atoms were not included. Refinement by full-matrix least squares on F led to a final conventional R value of 0.066 for 4656 reflections [$R' = 0.091$, $w = 1/\sigma(F)^2$, goodness of fit $S = 3.54$, highest and lowest residual densities 0.61 and −0.10 e Å^{-3}]. All calculations were performed on a VAX 4000-200 computer with the Enraf-Nonius MOLEN system.[17] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/465.

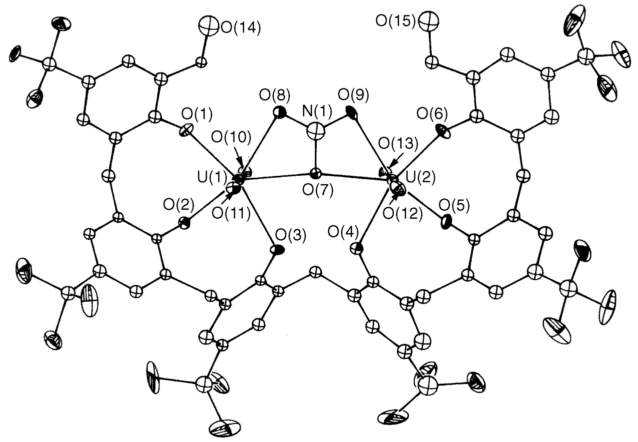

Fig. 1 Molecular unit of compound **1**, counter ions and solvent molecule omitted. Selected distances (Å) and angles (°); U(1)–O(1) 2.27(2), U(1)–O(2) 2.21(2), U(1)–O(3) 2.52(2), U(1)–O(7) 2.47(2), U(1)–O(8) 2.52(2), U(1)–O(10) 1.82(2), U(1)–O(11) 1.81(2), U(2)–O(4) 2.43(2), U(2)–O(5) 2.16(2), U(2)–O(6) 2.21(2), U(2)–O(7) 2.47(2), U(2)–O(9) 2.52(2), U(2)–O(12) 1.79(2), U(2)–O(13) 1.83(2), U(1) · · · U(2) 4.859(2); O(1)–U(1)–O(2) 82.6(6), O(2)–U(1)–O(3) 80.0(6), O(3)–U(1)–O(7) 66.8(5), O(7)–U(1)–O(8) 53.4(6), O(8)–U(1)–O(1) 77.3(7), O(10)–U(1)–O(11) 178.5(8), O(4)–U(2)–O(5) 80.0(6), O(5)–U(2)–O(6) 82.5(7), O(6)–U(2)–O(9) 76.7(7), O(9)–U(2)–O(7) 53.0(6), O(7)–U(2)–O(4) 67.9(6), O(12)–U(2)–O(13) 177.2(8), U(1)–O(7)–U(2) 159.9(8)

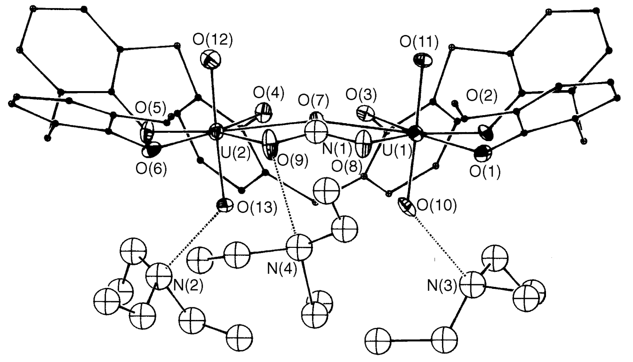

Fig. 2 Another view of compound **1**, including the triethylammonium ions (*tert*-butyl groups and methanol solvate molecule omitted). The atoms of the bis(hydroxymethyl)hexaphenol skeleton have been arbitrarily reduced for clarity. Hydrogen bonds in dashed lines. Hydrogen bonding distances (Å): N(2) · · · O(13) 2.81(2), N(3) · · · O(10) 2.81(2) and N(4) · · · O(9) 3.03(2)

of symmetrical bis-chelating co-ordination. Around each metal ion, the five bonding oxygen atoms are in a plane within ±0.07(2) Å [dihedral angle between these planes 14.3(5)°], the uranium ions being 0.013(1) and 0.027(1) Å from these mean planes. The O(uranyl)–U–O(ligand) angles are in the range 86.9–92.7° [mean value 90(2)°] indicative of the nearly perfect equatorial arrangement of the oxygen atoms within the uranyl co-ordination geometry. The presence of three triethylammonium ions, which form probable hydrogen bonds with two uranyl and one nitrate oxygen atoms as shown by the shortest contacts N(2)···O(13) 2.81(2), N(3)···O(10) 2.81(2) and N(4)···O(9) 3.03(2) Å (see Fig. 2), indicates that the two terminal, non-bonding, hydroxy groups have also been deprotonated. Triethylammonium ions bonded to uranyl oxygen atoms are also present in other calixarene complexes.[14,16]

The conformation of the hexaphenol in compound **1** can be described by the torsion angles around methylene bridges, as proposed for calixarenes;[19] it corresponds to the sequence $(-+,+-,-+,+-,-+)$, the same as that found in the two forms of the uranyl complex of *p-tert*-butylcalix[8]arene (4,11,18,25,32,39,46,53-octa-*tert*-butyl[1.$_8$]metacyclophane-7,14,21,28,35,42,49,56-octol), compound **2**,[14] which is $(+-,-+)_4$. The hexaphenol certainly being a rather flexible species in solution, may be fixed in a calixarene-like, pleated loop conformation, by the co-ordination to the metal ions, in an induced fit way. However, in the absence of structural data concerning the 'free' hexaphenol, we cannot exclude some kind of preorganization in solution due to intramolecular hydrogen bonding; such interactions have been described in the case of tetraphenols.[5–7] The O···O distances between adjacent phenolic units in **1** range from 2.49(2)–3.05(2) Å, the shorter distance between the two protonated atoms O(3) and O(4) is indicative of the formation of a hydrogen bond.

The binuclear uranyl co-ordination core geometry is very close to the one observed in compound **2**. The U(1)···U(2) separation and the U(1)–O(7)–U(2) angle are somewhat larger in compound **1** than in **2** [4.859(2) Å and 159.9(8)° instead of 4.503(2) Å and 147.2(9)° respectively], the hexaphenol being more 'flattened' than the calixarene. The doubly bidentate nitrate ion in **1** replaces two phenolic oxygen atoms and a bridging hydroxyl ion in **2**. Another difference between compounds **1** and **2** arises from the location of the triethylammonium ions hydrogen bonded to uranyl oxygen atoms: in **1** where the bending of the uranyl ions with respect to the mean plane of the molecule is less important than in **2**, the two oxygen atoms O(10) and O(13) are involved in the hydrogen bonding, whereas in **2** the other two oxygen atoms [corresponding to O(11) and O(12) in **1**] are involved. Notwithstanding these small differences, the analogy between compounds **1** and **2** is striking and confirms the conclusion of our previous study, that, in the case of *p-tert*-butylcalix[8]arene (whose conformation when 'free' is the same as when complexed) the perfect 'hole–size' match seems to play a more important role than the flexibility of the macrocycle.[14]

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