Actinide Complexes of the Calixarenes. Part 2.[1] Synthesis and Crystal Structure of a Novel Thorium(IV) Complex of *p-tert*-Butylcalix[8]arene *

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The synthesis and room-temperature single-crystal X-ray structure determination of a novel tetranuclear thorium complex with *p-tert*-butylcalix[8]arene, H_8L, has been achieved, the stoichiometry being assigned as $[Th_4(HL)(H_2L)(dmso)_4(OH)_3(OH_2)]\cdot dmso\cdot 2H_2O$ (dmso = Me_2SO). Crystals of the complex are triclinic, space group $P\bar{1}$, $a = 29.51(2)$, $b = 21.68(3)$, $c = 21.16(1)$ Å, $\alpha = 60.94(6)$, $\beta = 78.75(5)$, $\gamma = 87.75(8)°$ and $Z = 2$; the structure was refined to a residual of 0.079 for 16 903 'observed' $[I > 3\sigma(I)]$ reflections. Each calixarene unit, one with approximate *2* and the other approximate *mm* symmetry, is co-ordinated to two thorium atoms, the environment of each thorium comprising five ligand phenolic oxygen atoms, three being 'monodentate' and two bridging, with a monodentate O-bonded dmso entering through each cup of each ligand, and hydroxide groups variously bridging to the other thorium within the same ligand, and binding the two Th_2L systems together. The ^1H NMR spectrum has been rationalised in terms of the X-ray structure.

A recent review[2] highlights the facts that only limited investigation has been made of the chemistry of alkyl- and aryl-oxide complexes of the actinide elements and that the bulk of this work has focused on uranium(VI) complexes with unidentate alkoxide ligands.[3] Catecholate complexes[4,5] provide the only examples of bidentate aryl oxide systems, and the literature concerning multidentate and, in particular, macrocyclic aryl oxide ligands is exceedingly sparse. In a recent report[1] we have described the first single-crystal X-ray structural study of an actinide ion complex of a macrocyclic polyphenol, in this case the uranyl ion complex of bis(homooxa)-*p-tert*-butylcalix[4]arene, and solution equilibrium studies of sulphonated calixarenes have been described earlier by Shinkai *et al.*[6]

In the present paper we turn our attention to thorium(IV). Interest in this system was initially stimulated by the difficulties encountered in the characterisation of cerium(IV) complexes of *p-tert*-butylcalix[8]arene and it was anticipated that the interaction of Th^{IV} with this ligand might show some parallels with the cerium(IV) system.[5] Complexes of Th^{IV} are also relevant to any potential application of the calixarenes to areas such as the separation of the rare earths (lanthanides), since thorium is found naturally in association with these metals,[7] and organic-soluble complexes of Th^{IV} are of interest in their own right as materials for use in 'sol-gel' production of metal-oxide coatings.[8] The synthesis and structure of a 4:2 Th^{IV}:*p-tert*-butylcalix[8]arene complex (H_8L) characterised as $[Th_4(HL)(H_2L)(dmso)_4(OH)_3(OH_2)]\cdot dmso\cdot 2H_2O$ (dmso = dimethyl sulphoxide) is described below. We find the structure to be quite different to that of the only other crystallographically characterised metal(IV) complex of a calix[8]arene,[9] namely the bimetallic titanium(IV) complex of HL^{7-} which is more closely related to the lanthanide(III) complexes of *p-tert*-butylcalix[8]arene we have described.[10]

Experimental

Synthesis.—*p-tert*-Butylcalix[8]arene[11] and $Th(ClO_4)_4\cdot 12$-dmso[12] were prepared by literature methods.

In the normal atmosphere, *p-tert*-butylcalix[8]arene (H_8L) (0.75 g) was slurried in acetone (10 cm^3), triethylamine (0.5 cm^3) was added and the mixture was heated until the calixarene dissolved. A solution of $Th(ClO_4)_4\cdot 12dmso$ (1.83 g) in dmso (10 cm^3) was quickly added, resulting in a clear, colourless solution which was filtered and left to cool. Fine colourless needles slowly precipitated and were collected and dried in a desiccator to give a white powder. Yield: 0.51 g (41%) (Found: C, 54.4; H, 6.5; S, 6.4. $C_{184}H_{240}O_{24}S_4Th_4\cdot 5C_2H_6SO\cdot H_2O$ requires C, 54.20; H, 6.35; S, 6.70%). Recrystallisation of this material from acetone produced colourless cuboids which effloresced rapidly when dry to give a white powder (Found: C, 55.8; H, 6.2; S, 3.7. $C_{184}H_{240}O_{24}S_4Th_4\cdot C_2H_6SO\cdot 2H_2O$ requires C, 55.75; H, 6.30; S, 4.00%).

Structure Determination.—A unique data set was measured at ≈295 K within the limit $2\theta_{max} = 50°$ on a capillary-mounted specimen using an Enraf-Nonius CAD-4 diffractometer [2θ–θ scan mode, monochromatic Mo-Kα radiation ($\lambda = 0.7107_3$ Å)]. 23 985 Independent reflections were measured, 16 903 with $I > 3\sigma(I)$ being considered 'observed' and used in the large-block least-squares refinement after gaussian absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms, with a few exceptions described below where unreasonable refinement behaviour dictated use of the isotropic form; $(x,y,z,U_{iso})_H$ were included constrained at estimated values. Conventional residuals on $|F|$ at convergence were $R = 0.079$, $R' = 0.093$ [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$]. Neutral-atom complex scattering factors were employed;[13] computation used the XTAL 3.0 program system implemented by S. R. Hall.[14] Pertinent results are given in the figures and tables. The two ligands, about Th(1,2) and Th(1′,2′) respectively are designated L and L′.

Crystal data. $C_{184}H_{240}O_{24}S_4Th_4\cdot C_2H_6SO\cdot 2H_2O$, $M = 4006.5$, triclinic, space group $P\bar{1}$ (C_i^1, no.2), $a = 29.51(2)$, $b = 21.68(3)$, $c = 21.16(1)$ Å, $\alpha = 60.94(6)$, $\beta = 78.75(5)$, $\gamma = 87.75(8)°$, $U = 11\,582$ Å^3, D_c ($Z = 2$) = 1.15 g cm^{-3}, $F(000) = 8608$, $\mu_{Mo} = 25.2$ cm^{-1}, specimen 0.40 × 0.20 × 0.15 mm, $A^*_{min,max} = 1.34, 1.76$.

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* *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.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Abnormal features/variations in procedure. A number of atoms exhibited badly behaved thermal tensors and were refined with isotropic thermal parameters as follows: C(26), C(2), C(51)–C(56), C(71)–C(76) of L; C(21)–C(26) C(41)–C(46) of *L′; O(b′); all* Bu^t groups; lattice solvent molecules. The disordered Bu^t groups of ring 4 of L and rings 2 and 4 of L′ were each modelled as two rigid groups of three atoms. The co-ordinates of the Bu^t groups associated with ring 3 of L and ring 8 of L′ were unstable on refinement, presumably a consequence of less well resolved disorder and were included with estimated values. The lattice solvent molecules were modelled as two disordered water molecules, each with two envelopes, and one dmso molecule which was refined as a rigid group and may be partially populated [refined population 0.81(1)].

Calixarene rings are numbered *n* = 1–8 within each ligand, with O(*n*) pendant from C(*n*1) and co-ordinated to the thorium; C(*n*) is attached to C(*n*2) of the ring and bridges to C(*n* + 16) of ring *n* + 1. The Bu^t group is pendant from C(*n*4) by C(*n*41) with associated methyl carbons C(*n*42)–C(*n*44).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

A thorium(IV) complex of *p-tert*-butylcalix[8]arene (H_8L) has been readily synthesised as a dmso solvate in a manner identical to that used for the dmso solvates of the lanthanide(IV) complexes described elsewhere [15] and similar to those of dimethylformamide (dmf) solvates.[10,15] Elemental analysis of this complex, considered in conjunction with the nature of the structure described below, is consistent with the formulation $[Th_4(HL)(H_2L)(dmso)_4(OH)_3(OH_2)]\cdot5dmso\cdot H_2O$; other formulations based on the microanalytical data alone are possible of course, particularly with respect to the distribution of the phenolic and OH_x protons. This complex was apparently stable in the laboratory atmosphere and was appreciably soluble in acetone; recrystallisation from acetone gave well formed, colourless, cuboids which, although extremely efflorescent, were suitable for X-ray diffraction studies when mounted in capillaries wet with mother-liquor. Elemental analysis of these crystals indicated that the complex had changed in composition upon recrystallisation, and this has been rationalised in terms of changes in the lattice solvent molecules. It has been shown in a number of systems, however, that alkoxide and aryl oxide complexes of highly charged cations can readily form well defined, partial hydrolysis products.[2,16] Certainly, no rigorous precautions were taken to exclude water from the system, and, given the hygroscopicity of the solvents used, it is possible that appreciable amounts of water were present. It is possible, therefore, that a more fundamental change may have occurred in the thorium(IV) complex, with hydrolysis of the initial product resulting in the formation of the hydroxothorium oligomer described below.

The results of the structure determination clearly define the principal features of the complex molecule, although high thermal motion and disorder are observed at the periphery. Lattice solvent molecules were modelled as two disordered waters (two envelopes each) and one dmso, seemingly not fully populated [refined population 0.81(1)]. The complex molecule is centred about a tetranuclear core of thorium(IV) atoms which is co-ordinated to two *p-tert*-butylcalix[8]arene ligands, and can be reasonably formulated as $[Th_4(HL)(H_2L')(dmso)_4(OH)_3(OH_2)]$. Distribution of the residual protons in this formulation was (cautiously) made on the basis of Th–O bond distances, and the assumption that the oxidation state of the metal was not likely to vary. Ligands comprising a single residue were assumed to be OH_x moieties; those bridging between metal centres were assumed to be hydroxyl groups and the one terminal ligand was assigned as a water oxygen atom. The data upon which this proposed formulation is based will be discussed in detail below.

Fig. 1(*a*) shows the complex molecule together with a stylised representation [Fig. 1(*b*)] which emphasises the conformations of the calixarenes and their positions relative to the metal atoms. It is obvious that the two calixarene ligands, L and L′, are in notably different conformations; L is found in a 'propeller' conformation with approximate *2* symmetry, while L′ assumes a 'crown' conformation with approximate *mm* symmetry [Fig. 1(*c*)]. The two calixarenes form four cavities, each defined by four aryl rings. Each of these is associated with a thorium atom and is filled by a co-ordinatively included dmso molecule so that each thorium(IV) atom is bound to one dmso oxygen atom.

The familiar propeller conformation of L is more clearly seen in Fig. 1(*c*), which shows the similarity of this portion of the complex to the $[Ln_2(H_2L)]$ complexes described elsewhere.[10,15,17] Thus, there is a Th_2O_3 core, with two bridging phenolic O atoms and a bridging hydroxyl O atom [rather than the dmso or dmf bridging O atom as found in the lanthanide(III) complexes]. The disposition of the O-donor atoms about Th(1) shown in Table 2(*a*) shows a similar hierarchy of bond distances to that observed in the lanthanide(III) complexes; for example, Th(1)–O(3), at 2.81(2) Å, is the longest metal–oxygen separation involving Th(1) suggesting that a proton resides on O(3), once again at the 'tip' of the propeller. The co-ordination environment of Th(2) is somewhat different, as might be expected since the phenolic donor atoms O(7,8) are bridging between Th(2),Th(1′) and Th(2),Th(2′) respectively. In this case, it appears that the five phenoxide O atoms about Th(2) are all deprotonated, since four are bridging to other thorium atoms (with no outstandingly long Th–O distances) and the other lies close to Th(2); Th(2)–O(6) is 2.16(1) Å. The observation of the propeller conformation for seemingly H_2L^{6-} and HL^{7-} suggests that this may be a favoured configuration for manifold deprotonated calix[8]arenes, though there are differences in detail between the rare-earth, thorium and titanium systems and of course the two calix[8]arene ligands in the thorium cluster do not both adopt a propeller form.

The second calixarene ligand, L′, assumes a crown conformation bent about the C(1′) ··· C(5′) line [Fig. 1(*c*)]. The two thorium atoms closely associated with this ligand, Th(1′,2′), are not bridged by any of the phenoxide O atoms, although they are bridged by one hydroxyl O atom [Th(1′,2′)–O(b′) 2.48(2) and 2.47(1) Å]. It is notable that the separation of these thorium atoms, at 4.851(6) Å, is significantly greater than the Th(1) ··· Th(2) distance of 3.828(4) Å associated with L. Atoms Th(1′) and Th(2′) are co-ordinated to four phenoxide O atoms with rather regular bond distances (Table 2); the longest of these distances are Th(1′)–O(4′) and Th(2′)–O(5′) at 2.48(2) and 2.57(2) Å respectively. It is proposed that these oxygen atoms are protonated so that L′ is a hexaanion; it is notable that the O(4′) ··· O(5′) separation [2.58(2) Å)] is the closest contact of calixarene oxygen atoms in the complex, with the possible implication of a hydrogen bond. Ligand L′ has quasi-*mm* symmetry although the disposition of L ensures that such symmetry does not extend to the complex as a whole.

Each calixarene ligand forms two groups of four nearly coplanar phenolic oxygen atoms, each group being associated with one of the thorium atoms. The dihedral angles between the O_4 planes and the phenyl ring planes are given in Table 3. These figures reflect the unsymmetrical nature of both calixarenes. The thorium atoms all lie out of their associated O_4 planes, away from the ligand cavity, at distances ranging from 0.42(1) to 0.556(9) Å. The dihedral angles between the two O_4 planes of L and L′ are 75.1(5)° and 64.2(5)° respectively. The torsion angles of the two *p-tert*-butylcalix[8]arene ligands (Table 3) show qualitatively similar sequences, with changes in sign occurring when the angle involves the methylene carbon atoms which link the cavities [C(1,5) for L, C(4′,8′) for L′], as has been observed in the lanthanide(III)–*p-tert*-butylcalix[8]arene complexes.[15]

Fig. 1(*d*) shows the core of the complex, emphasising the rather complex Th–O interactions which bind the conglomerate. The closest Th ··· Th contacts all involve Th(2)

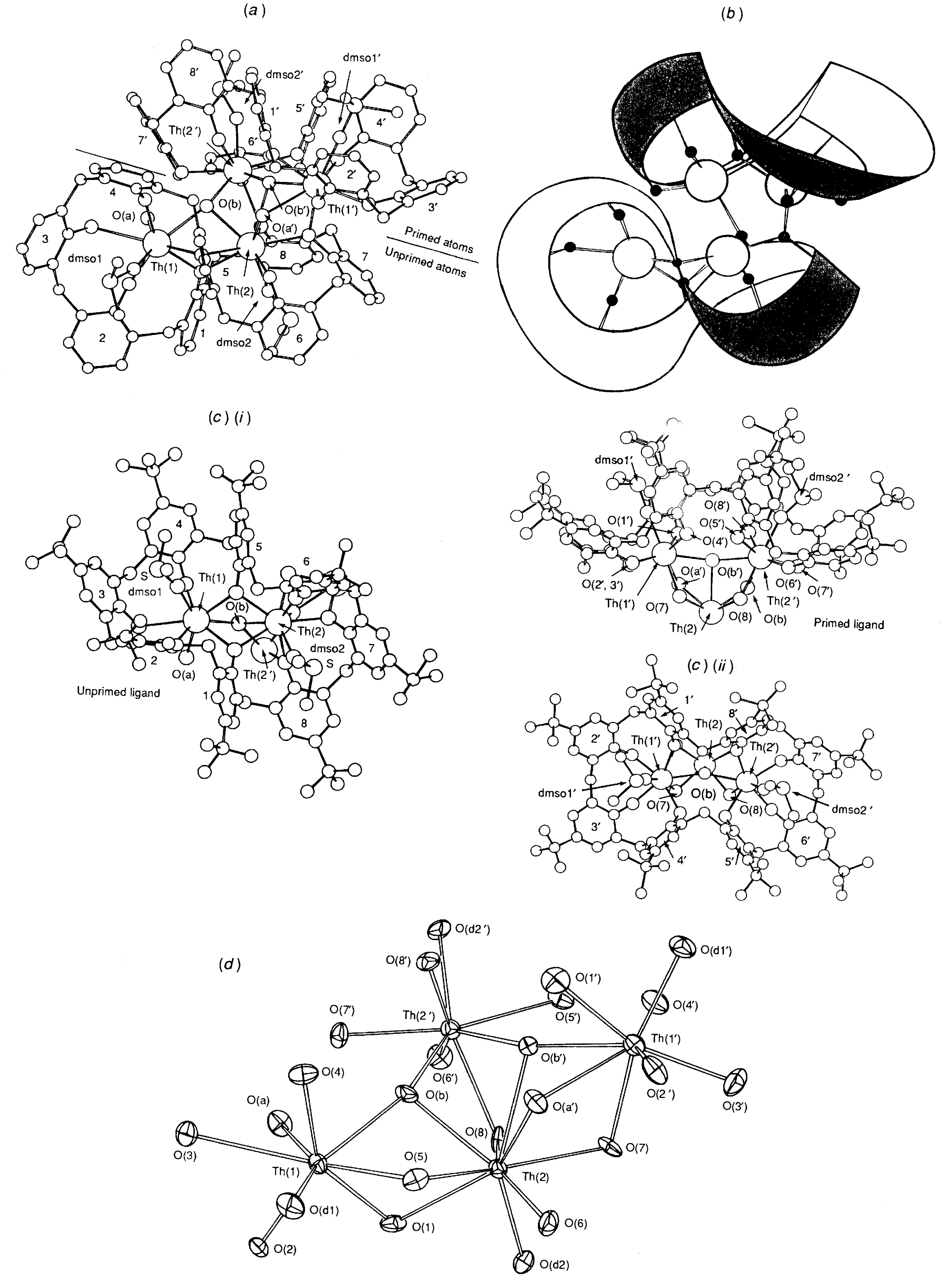

Fig. 1 (*a*) The complex molecule showing spheres of arbitrary radius for the non-hydrogen atoms; Bu^t groups are omitted. Ring labelling is shown. (*b*) Stylised representation of the molecule. (*c*) (*i*), (*ii*) Fragmentation of the total molecule showing affiliations of the thorium atoms with each ligand, and associated dmso, hydroxyl and water moieties. The Bu^t groups are shown with major constituents for those that are disordered. Two views are shown for the primed ligand. (*d*) The 'core' of the complex, showing the linking of the tetranuclear aggregate (20% thermal envelopes are shown)

Table 1 Non-hydrogen atom coordinates (primed atoms for the second column) *

Atom	*x*	*y*	*z*	*x*	*y*	*z*
Th(1)	0.239 39(4)	0.341 84(5)	0.094 01(5)	0.227 35(4)	0.052 78(5)	0.027 57(6)
Th(2)	0.188 33(3)	0.227 46(5)	0.029 61(5)	0.308 48(4)	0.284 91(5)	−0.107 07(5)
O(1)	0.186 5(5)	0.352 4(7)	0.015 4(8)	0.285 2(6)	0.048 9(9)	0.095 5(9)
C(11)	0.163 6(8)	0.409(1)	−0.020(1)	0.318 6(9)	0.009(1)	0.133(1)
C(12)	0.127 4(9)	0.434(1)	0.018(1)	0.301(1)	−0.047(1)	0.212(1)
C(13)	0.100 7(9)	0.490(1)	−0.019(1)	0.337(1)	−0.084(1)	0.245(2)
C(14)	0.109 0(8)	0.524(1)	−0.089(1)	0.382(1)	−0.073(1)	0.208(2)
C(141)	0.084(1)	0.586(2)	−0.133(2)	0.424(1)	−0.121(2)	0.249(2)
C(142)	0.049(2)	0.610(3)	−0.082(3)	0.469(1)	−0.101(2)	0.207(2)
C(143)	0.051(2)	0.562(3)	−0.161(3)	0.408(2)	−0.130(2)	0.328(3)
C(144)	0.103(2)	0.659(3)	−0.182(3)	0.410(2)	−0.195(2)	0.261(2)
C(15)	0.147 7(9)	0.508(1)	−0.129(1)	0.397(1)	−0.023(1)	0.136(1)
C(16)	0.175 1(9)	0.451(1)	−0.097(1)	0.364 2(8)	0.021(1)	0.094(2)
C(1)	0.116 2(8)	0.397(1)	0.105(1)	0.249(1)	−0.065(1)	0.251(1)
O(2)	0.204 7(5)	0.438 9(8)	0.083 2(8)	0.191 3(6)	−0.024 8(7)	0.146 1(9)
C(21)	0.173 2(9)	0.461(1)	0.120(1)	0.197 2(9)	−0.091(1)	0.188(1)
C(22)	0.183 7(8)	0.499(1)	0.153(1)	0.170 9(9)	−0.142(1)	0.185(1)
C(23)	0.151 4(8)	0.516(1)	0.193(1)	0.182(1)	−0.217(2)	0.232(2)
C(24)	0.106 1(9)	0.498(1)	0.204(1)	0.214(1)	−0.238(2)	0.278(2)
C(241)	0.068(1)	0.515(2)	0.258(2)	0.225(1)	−0.320(2)	0.323(2)
C(242)	0.084(2)	0.580(3)	0.264(3)	0.248(1)	−0.335(3)	0.382(2)
C(243)	0.029(2)	0.559(3)	0.204(3)	0.174 4(2)	−0.361(3)	0.354(2)
C(244)	0.032(2)	0.468(3)	0.304(3)	0.250(1)	−0.338(3)	0.264(1)
C(245)				0.203(1)	−0.365(3)	0.289(2)
C(246)				0.274 0(3)	−0.326(3)	0.314(2)
C(247)				0.196(1)	−0.343(3)	0.397(2)
C(25)	0.093 9(9)	0.459(1)	0.173(1)	0.236(1)	−0.186(2)	0.283(2)
C(26)	0.128 7(7)	0.442(1)	0.135(1)	0.225 5(9)	−0.118(1)	0.238(1)
C(2)	0.232(1)	0.524(1)	0.140(2)	0.134 7(9)	−0.121(1)	0.138(2)
O(3)	0.298 0(6)	0.434 9(9)	0.103 8(9)	0.175 1(6)	−0.003 4(9)	0.006(1)
C(31)	0.294 5(9)	0.426(1)	0.176(1)	0.167 7(9)	−0.061(1)	0.000(2)
C(32)	0.321 3(9)	0.380(1)	0.222(1)	0.177(1)	−0.056(1)	−0.071(1)
C(33)	0.316(1)	0.374(1)	0.292(1)	0.172(1)	−0.116(1)	−0.074(2)
C(34)	0.286 8(9)	0.415(1)	0.313(1)	0.158(1)	−0.177(2)	−0.017(2)
C(341)	0.282 6(–)	0.405 8(–)	0.392 9(–)	0.153(1)	−0.247(2)	−0.019(2)
C(342)	0.275 5(–)	0.330 1(–)	0.445 0(–)	0.171(1)	−0.238(2)	−0.089(2)
C(343)	0.233 3(–)	0.419 5(–)	0.418 6(–)	0.104(2)	−0.273(2)	0.008(2)
C(344)	0.296 4(–)	0.475 4(–)	0.380 3(–)	0.176(2)	−0.300(2)	0.036(2)
C(35)	0.261 2(9)	0.462(1)	0.264(1)	0.147(1)	−0.183(1)	0.052(2)
C(36)	0.263 6(9)	0.473(1)	0.189(1)	0.148 6(8)	−0.122(1)	0.066(2)
C(3)	0.352 9(8)	0.333(1)	0.201(1)	0.199(1)	0.011(1)	−0.133(1)
O(4)	0.295 4(5)	0.277 4(8)	0.151 1(9)	0.263 5(6)	0.093 8(8)	−0.103 3(8)
C(41)	0.307 3(8)	0.233(1)	0.215(1)	0.280 7(8)	0.052(1)	−0.136(1)
C(42)	0.291 5(9)	0.164(1)	0.255(1)	0.328 3(9)	0.052(1)	−0.156(1)
C(43)	0.304(1)	0.120(1)	0.318(1)	0.349 9(9)	0.010(1)	−0.190(2)
C(44)	0.330(1)	0.144(1)	0.347(2)	0.320 0(9)	−0.028(1)	−0.200(1)
C(441)	0.342(1)	0.092(2)	0.427(2)	0.340(1)	−0.070(2)	−0.240(2)
C(442)	0.353(3)	0.022(2)	0.432(2)	0.354(3)	−0.026(1)	−0.325(1)
C(443)	0.385(2)	0.121(3)	0.444(2)	0.386(1)	−0.104(4)	−0.212(3)
C(444)	0.299 7(9)	0.085(4)	0.487(2)	0.306(2)	−0.133(4)	−0.220(3)
C(445)	0.312(3)	0.021(4)	0.474(2)	0.394(1)	−0.049(3)	−0.276(3)
C(446)	0.393 3(8)	0.075(6)	0.417(3)	0.318(2)	−0.067(3)	−0.304(3)
C(447)	0.334(4)	0.134(3)	0.469(4)	0.336(2)	−0.147(1)	−0.178 2(9)
C(45)	0.346 6(9)	0.214(1)	0.306(2)	0.276(1)	−0.029(2)	−0.185(2)
C(46)	0.335 7(9)	0.258(1)	0.241(1)	0.249 0(9)	0.012(1)	−0.149(1)
C(4)	0.257 7(9)	0.134(1)	0.225(1)	0.360 0(8)	0.106(1)	−0.161(1)
O(5)	0.193 0(5)	0.233 3(8)	0.145 7(8)	0.303 0(5)	0.219 5(8)	−0.179 4(8)
C(51)	0.176 9(8)	0.176(1)	0.217(1)	0.334 8(7)	0.228(1)	−0.241(1)
C(52)	0.130 0(9)	0.165(1)	0.247(1)	0.333 4(8)	0.282(1)	−0.308(1)
C(53)	0.116(1)	0.113(2)	0.324(2)	0.366 9(8)	0.283(1)	−0.368(1)
C(54)	0.147(1)	0.074(1)	0.359(2)	0.397 4(9)	0.234(1)	−0.360(1)
C(541)	0.125(1)	0.027(2)	0.446(2)	0.434(1)	0.238(2)	−0.426(2)
C(542)	0.083(2)	−0.005(3)	0.458(3)	0.412(2)	0.205(3)	−0.458(3)
C(543)	0.157(2)	0.026(3)	0.481(3)	0.482(2)	0.224(3)	−0.415(3)
C(544)	0.145(2)	−0.044(3)	0.454(3)	0.437(2)	0.303(3)	−0.495(3)
C(55)	0.190(1)	0.079(1)	0.330(2)	0.395 7(9)	0.178(1)	−0.295(1)
C(56)	0.208 8(9)	0.130(1)	0.256(1)	0.364 8(8)	0.176(1)	−0.234(1)
C(5)	0.091(1)	0.210(1)	0.202(2)	0.299 2(9)	0.340(1)	−0.322(1)
O(6)	0.128 7(5)	0.161 8(9)	0.108 8(9)	0.306 8(5)	0.373 6(8)	−0.216 9(8)
C(61)	0.085 2(9)	0.143(1)	0.144(1)	0.326 8(8)	0.421(1)	−0.287(1)
C(62)	0.062 5(8)	0.097(1)	0.135(1)	0.348 3(8)	0.483(1)	−0.302(1)
C(63)	0.016(1)	0.078(1)	0.166(1)	0.370 8(9)	0.529(1)	−0.373(1)
C(64)	−0.008 3(8)	0.105(1)	0.214(1)	0.367 7(9)	0.516(1)	−0.429(1)
C(641)	−0.062(1)	0.081(2)	0.250(2)	0.392(1)	0.568(2)	−0.507(2)

Table 1 (*continued*)

Atom	*x*	*y*	*z*	*x*	*y*	*z*
C(642)	−0.059(2)	0.010(3)	0.310(3)	0.417(2)	0.631(2)	−0.518(3)
C(643)	−0.088(2)	0.073(2)	0.203(3)	0.357(2)	0.591(2)	−0.564(3)
C(644)	−0.078(2)	0.123(3)	0.282(3)	0.421(2)	0.530(3)	−0.537(4)
C(65)	0.015 8(9)	0.148(1)	0.227(2)	0.344 2(9)	0.455(1)	−0.413(1)
C(66)	0.061 7(9)	0.165(1)	0.194(1)	0.323 5(8)	0.407(1)	−0.342(1)
C(6)	0.085 0(8)	0.063(1)	0.086(2)	0.352 1(9)	0.498(1)	−0.239(1)
O(7)	0.172 9(5)	0.142 9(8)	−0.007 6(8)	0.337 4(5)	0.377 0(8)	−0.094 7(8)
C(71)	0.133 6(8)	0.145(1)	−0.040(1)	0.380 7(9)	0.404(1)	−0.124(1)
C(72)	0.138 2(8)	0.184(1)	−0.114(1)	0.416 5(8)	0.380(1)	−0.090(1)
C(73)	0.103 3(8)	0.188(1)	−0.148(1)	0.458 5(9)	0.409(1)	−0.119(1)
C(74)	0.061 4(9)	0.152(1)	−0.101(1)	0.471 7(9)	0.463(2)	−0.185(2)
C(741)	0.019(1)	0.161(2)	−0.144(2)	0.520(1)	0.506(2)	−0.225(2)
C(742)	−0.019(2)	0.092(3)	−0.078(3)	0.548(2)	0.517(2)	−0.185(3)
C(743)	−0.001(2)	0.223(3)	−0.161(3)	0.525(2)	0.566(3)	−0.306(3)
C(744)	0.030(4)	0.115(6)	−0.170(6)	0.542(2)	0.459(3)	−0.243(3)
C(75)	0.056 3(8)	0.110(1)	−0.026(1)	0.438(1)	0.494(2)	−0.228(2)
C(76)	0.094 0(8)	0.110(1)	0.004(1)	0.391 5(8)	0.465(1)	−0.197(1)
C(7)	0.184 3(9)	0.220(1)	−0.163(1)	0.407 2(8)	0.318(1)	−0.015(1)
O(8)	0.222 2(5)	0.291 1(7)	−0.098 7(7)	0.348 7(5)	0.216 0(8)	−0.013 9(8)
C(81)	0.204 2(8)	0.332(1)	−0.158(1)	0.392 1(8)	0.200(1)	−0.008(1)
C(82)	0.201 3(8)	0.403(1)	−0.183(1)	0.409 1(8)	0.132(1)	0.006(1)
C(83)	0.185 9(9)	0.441(1)	−0.246(1)	0.453 6(9)	0.118(2)	0.013(2)
C(84)	0.168(1)	0.413(1)	−0.285(1)	0.483(1)	0.164(2)	0.010(2)
C(841)	0.148(1)	0.455(2)	−0.357(2)	0.540(1)	0.159(2)	0.027(2)
C(842)	0.180(2)	0.460(3)	−0.419(3)	0.562 9(−)	0.199 2(−)	0.052 8(−)
C(843)	0.139(2)	0.529(2)	−0.373(3)	0.535 7(−)	0.067 6(−)	0.082 9(−)
C(844)	0.106(2)	0.418(3)	−0.354(3)	0.574 8(−)	0.168 7(−)	−0.051 5(−)
C(85)	0.169 0(9)	0.343(1)	−0.258(1)	0.469 0(9)	0.230(2)	0.001(1)
C(86)	0.186 7(8)	0.302(1)	−0.194(1)	0.421 3(8)	0.246(1)	−0.008(1)
C(8)	0.217 0(8)	0.438(1)	−0.144(1)	0.377 9(9)	0.077(1)	0.017(1)
dmso(1)						
O	0.206 1(6)	0.309 8(9)	0.218 9(9)	0.275 5(6)	−0.037 6(9)	0.032 1(9)
S	0.195 6(4)	0.308 4(6)	0.290 4(5)	0.308 0(3)	−0.092 0(5)	0.028 7(5)
C(1)	0.209(1)	0.229(2)	0.351(2)	0.312(1)	−0.152(2)	0.117(2)
C(2)	0.144(1)	0.305(2)	0.315(2)	0.277(1)	−0.144(2)	0.007(2)
dmso(2)						
O	0.126 8(6)	0.284 6(9)	−0.028(1)	0.383 7(5)	0.288 3(9)	−0.172 8(9)
S	0.078 7(3)	0.282 9(5)	−0.042 3(5)	0.433 8(3)	0.316 5(5)	−0.207 1(5)
C(1)	0.041(2)	0.301(2)	0.016(2)	0.438(1)	0.354(2)	−0.302(2)
C(2)	0.078(1)	0.369(2)	−0.122(2)	0.466(1)	0.249(2)	−0.194(2)
OH_x						
O(a)	0.290 4(6)	0.425 1(8)	−0.021 0(8)	0.210 6(6)	0.110 2(8)	0.116 8(9)
O(b)	0.266 3(5)	0.278 2(8)	0.017 3(8)	0.264 0(5)	0.171 8(7)	−0.017 9(7)
O(c1)	0.401(1)	0.111(2)	0.197(2)	0.324(2)	−0.322(3)	0.094(3)
O(c2)	0.454(2)	0.087(3)	0.241(3)	0.350(2)	−0.363(3)	0.062(3)
dmso(3)						
O	0.306(2)	−0.449(2)	−0.034(2)			
S	0.277 4(6)	−0.387 5(9)	−0.080 8(8)			
C(1)	0.223 0(5)	−0.413(4)	−0.082(3)			
C(2)	0.312(2)	−0.332(2)	−0.174(1)			

* Populations not equal to unity are as follows: C(442)–C(444) 0.53(2); C(445)–C(447) 1–0.53(2); C(242′)–C(244′) 0.55(2); C(245′)–C(247′) 1–0.55(2); C(442′)–C(444′) 0.44(3); C(445′)–C(447′) 1–0.44(3); O(c1) 0.42(3); O(c2) 1–0.42(3); O(c1′) 0.47(4); O(c2′) 1–0.47(4); dmso (3) 0.81(1).

[Th(2) ··· Th(1,1′,2′) 3.828(4), 3.933(5), 3.916(2) Å]. These distances are comparable to the 3.960(3) Å separation of the thorium atoms observed in a trinuclear dihydroxo(5,10,15,20-tetraphenylporphyrinato)thorium(IV) complex.[18] The central nature of Th(2) in the complex is also reflected by the fact that it is co-ordinated to all the bridging oxygen atoms, resulting in co-ordination to nine O-donor atoms rather than eight, as observed for the other thorium atoms. The four bridging phenoxide O atoms are derived from L, bridging various pairs of Th atoms with Th–O distances ranging from 2.38(1) to 2.57(2) Å and Th–O–Th angles varying from 99.9(1) to 109.8(7)° (Table 2). Analogous bond lengths in a binuclear thorium(IV) complex of a compartmental Schiff-base ligand vary from 2.41 to 2.50 Å.[19] The hydroxy atom O(a′) bridges between Th(2) and Th(1′) although the Th–O bond distances vary significantly [Th(2,1′)–O(a′) 2.47(1) and 2.69(2) Å]. This compares with a Th–O bond distance of 2.46(2) Å found for the bridging hydroxyl groups in the trinuclear complex mentioned above.[18] The two remaining bridging O atoms each interact with three Th atoms. The hydroxyl atom O(b) lies between Th(1,2,2′) with quite regular Th–O bond lengths [O(b)–Th(1,2,2′) 2.60(2), 2.50(2) and 2.62(2) Å], but varying angles about the O atom [Th(2)–O–Th(1,2′) 97.3(5) and 99.8(7); Th(1)–O–Th(2′) 149.1(6)°]. The geometry about O(b′) is similar to this with respect to the Th–O–Th angles (Table 2), although the Th–O bond distances have a greater range [O(b′)–Th(2,1′,2′) 2.75(2),

Table 2 Thorium environments in the thorium(IV) complex of *p*-*tert*-butylcalix[8]arene *

(*a*) Th(1)

Atom	*r*	O(2)	O(3)	O(4)	O(5)	O(d1)	O(a)	O(b)
O(1)	2.42(2)	79.4(7)	136.2(4)	144.3(7)	69.4(5)	117.0(6)	84.8(5)	67.5(5)
O(2)	2.23(2)		68.0(6)	136.3(8)	119.0(5)	77.2(6)	83.7(5)	139.6(6)
O(3)	2.81(2)			73.2(6)	152.6(5)	84.1(6)	63.9(6)	123.4(5)
O(4)	2.26(2)				88.1(6)	79.7(6)	96.9(5)	79.2(6)
O(5)	2.40(2)					72.8(7)	140.0(7)	70.2(5)
O(d1)	2.39(2)						147.2(7)	137.7(5)
O(a)	2.44(1)							71.8(6)
O(b)	2.60(2)							

(*b*) Th(2)

Atom	*r*	O(5)	O(6)	O(7)	O(8)	O(d2)	O(b)	O(a′)	O(b′)
O(1)	2.57(2)	64.9(5)	110.5(6)	152.1(5)	82.5(5)	71.3(7)	66.8(5)	137.2(7)	125.6(4)
O(5)	2.55(2)		76.5(7)	140.2(4)	137.1(5)	115.8(7)	69.6(5)	74.0(6)	113.3(5)
O(6)	2.16(1)			74.2(7)	144.1(7)	77.8(5)	143.4(6)	68.6(6)	122.1(6)
O(7)	2.41(2)				79.7(5)	83.5(7)	126.3(6)	70.6(6)	63.5(5)
O(8)	2.38(1)					75.1(5)	72.4(5)	124.4(6)	63.6(4)
O(d2)	2.36(2)						129.3(5)	142.0(6)	130.3(6)
O(b)	2.50(2)							88.7(5)	63.1(6)
O(a′)	2.47(1)								61.2(5)
O(b′)	2.75(2)								

(*c*) Th(1′)

Atom	*r*	O(1′)	O(2′)	O(3′)	O(4′)	O(d1′)	O(a′)	O(b′)
O(7)	2.40(2)	122.9(7)	101.1(5)	81.8(6)	91.3(5)	162.9(7)	67.0(6)	67.9(5)
O(1′)	2.41(2)		78.7(6)	149.8(6)	110.2(6)	73.1(7)	61.1(6)	68.0(5)
O(2′)	2.29(1)			79.5(7)	157.5(7)	87.6(6)	66.2(6)	127.1(7)
O(3′)	2.24(2)				83.8(7)	85.4(7)	126.4(6)	142.1(5)
O(4′)	2.48(2)					76.0(6)	136.3(5)	75.0(6)
O(d1′)	2.35(2)						130.2(4)	118.3(5)
O(a′)	2.69(2)							61.9(5)
O(b′)	2.48(2)							

(*d*) Th(2′)

Atom	*r*	O(5′)	O(6′)	O(7′)	O(8′)	O(d2′)	O(b)	O(b′)
O(8)	2.52(2)	84.5(6)	80.1(5)	109.4(6)	128.4(4)	150.9(6)	68.3(5)	66.1(4)
O(5′)	2.57(2)		78.8(6)	152.7(4)	107.6(6)	72.5(6)	137.5(5)	74.0(5)
O(6′)	2.19(1)			80.5(6)	150.6(5)	78.3(5)	124.7(6)	138.1(6)
O(7′)	2.35(2)				82.7(6)	85.9(6)	69.6(5)	132.9(6)
O(8′)	2.33(2)					76.7(5)	70.1(5)	69.6(5)
O(d2′)	2.36(1)						140.6(6)	121.4(5)
O(b)	2.62(2)							65.5(6)
O(b′)	2.47(1)							

(*e*) Th–O–Th angles (°) and Th · · · Th distances (Å)

Th(1)–O(1,5,b)–Th(2) 99.9(5), 101.2(5), 97.3(5)
Th(1)–O(b)–Th(2′) 149.1(6)
Th(2)–O(7,a′,b′)–Th(1′) 109.8(7), 99.3(6), 97.5(4)
Th(2)–O(8,b,b′)–Th(2′) 106.0(6), 99.8(7), 97.2(5)
Th(1′)–O(b′)–Th(2′) 157.2(8)
Th(2) · · · Th(1,1′,2′) 3.828(4), 3.933(5), 3.916(2) Å; Th(1′) · · · Th(2′) 4.851(6)

* *r* is the Th–O distance (Å) and the other entries in the matrix are the angles (°) subtended at the thorium by the relevant atoms at the head of the row and column. O(*n*) are phenolic oxygen atoms of L, O(*n*′) are phenolic oxygen atoms of L′, O(d*n*) are dmso oxygen atoms, O(a) is a terminal OH_x ligand, and O(b,a′,b′) are bridging OH_x ligands.

2.48(2) and 2.47(1)°]. The possibility that these two ligands may be fully deprotonated oxo atoms was considered, but comparison of these Th–O bond lengths with those found in a system apparently containing a bridging oxo atom [Th–O 2.13(2) Å; ten-co-ordinate Th^{IV} [20]] suggests that shorter bond distances would probably be expected. The unidentate oxygen atom, presumably water, O(a), is co-ordinated to Th(1) with a bond length of 2.44(1) Å, similar to the Th–OH_2 distance of 2.453(7) Å in the eight-co-ordinate complex [$ThCl_4(OHEt)_3(OH_2)$].[21] The result of these Th–O interactions, with respect to the metal environments, is that the metal atoms Th(1,1′,2′) are eight-co-ordinate, interacting with five phenol O atoms, one dmso O atom and two OH_x moieties, and Th(2) is nine-co-ordinate interacting with all of the above and an additional OH_x moiety.

The formation of tetrameric conglomerates appears to be a common feature of the chemistry of thorium, especially in neutral and basic aqueous solutions.[22] Thus, a solution of '$ThO(ClO_4)_2$' in water is reported to form a tetrameric species which has been tentatively formulated as $[Th_4(OH)_6]^{10+}$,[23] and the structure of one form of $ThO_2{\cdot}2H_2O$ is described in terms of hydroxyl-bridged Th_4 tetrahedra which are linked by hydrogen bonding between the hydroxyl groups.[24] Studies of hydrolysed thorium nitrate solutions using large- and small-angle X-ray scattering techniques are consistent with the presence of small conglomerates with structures based on face-sharing tetrahedra.[25] The Th atoms are found to be joined by double oxygen bridges and the Th · · · Th distances were estimated to be 4.0 Å. Given the ready formation of such species in basic solutions, it is possible that the formation of the thorium(IV)–*p*-*tert*-butylcalix[8]arene complex involves inter-

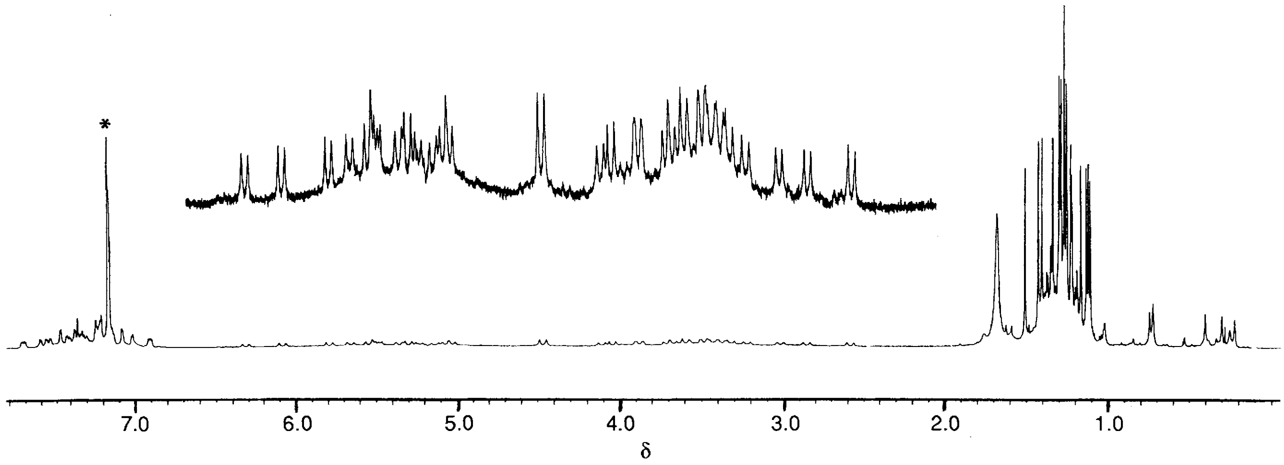

Fig. 2 The 300 MHz ^1H NMR spectrum of the complex in C_6D_6, * indicates residual solvent proton resonance

Table 3 Macrocycle parameters in the thorium(IV) complex of *p-tert*-butylcalix[8]arene*

	L			L′		
n	+	−	φ	+	−	φ
1	111	104	59.4(7)^b	86	114	46.8(8)^c
2	−84	−63	52.8(7)^a	104	−103	61.2(9)^c
3	−106	93	74.7(8)^a	93	−94	53.7(9)^c
4	−98	89	46.1(8)^a	−82	−110	59.2(8)^c
5	116	107	58.9(8)^a	109	89	60.7(7)^d
6	−72	−71	38.1(8)^b	82	−90	42.3(8)^d
7	−105	97	70.2(7)^b	102	−103	68.5(8)^d
8	−102	93	60.1(7)^b	−105	−94	54.4(8)^d

* Torsion angles: +, C(*n*1)–C(*n*2)–C(*n*)–C(*n* + 16); −, C(*n*1)–C(*n*6)–C(*n* − 1)–C(*n* − 12); error estimates are typically 3°. φ is the dihedral angle between the phenyl ring plane (*n*) and its associated phenolic O_4 plane (O_4 groupings are indicated by the superscript letters in this column) δ is deviation of atom from the plane: plane (a) χ^2 0.7, δ(O) < 0.02 Å, δ[Th(1)] 0.521(9) Å; plane (b) χ^2 3.0, δ(O) < 0.03 Å, δ[Th(2)] 0.556(9) Å plane (c) χ^2 15.9, 4δ(O) −0.04, 0.05, −0.07, 0.03 Å, δ[Th(1′)] 0.42(1) Å; plane (d) χ^2 5.1, δ(O) < 0.03 Å, δ[Th(2′)] 0.498(9) Å.

action of the calixarene with a thorium conglomerate already present in solution. The changes observed upon recrystallisation of the complex can then be related to a change in the structure of such a conglomerate, perhaps induced by constraints of the calixarene ligands.

The ^1H NMR spectrum of this thorium(IV) complex is complicated and has not been fully assigned (Fig. 2). There are at least sixteen resonances that can be assigned to Bu^t groups and as many pairs of doublets arising from methylene protons. The splitting of the methylene resonances into pairs of doublets indicates that the calixarene ligands are rigid in solution at room temperature on the NMR time-scale.[11] The appearance of resonances in the range δ 0.2–0.8 is consistent with the presence of 'co-ordinatively included' dmso molecules, where the resonances of the dmso methyl groups are shifted upfield as a consequence of their proximity to the aryl rings of the calixarene (as has been observed in other systems[9,15]). Such a complex spectrum would be expected if the structure observed in the solid state is maintained in solution, although it is possible that two or more species are present. Solutions of the thorium(IV) complex in benzene appear to be stable in the normal atmosphere, unlike solutions of lanthanide(III) complexes of *p-tert*-butylcalix[8]arene in non-polar solvents which are extremely sensitive to exposure to the atmosphere.[15]

A cerium(IV) complex of *p-tert*-butylcalix[8]arene has been synthesised by the method described here for the thorium(IV) complex, but unfortunately the deep purple complex consistently displays crystal morphologies unsuited to structure determination by X-ray diffraction. Similarities between the two complexes are apparent, such as stability in the atmosphere and solubility in acetone, although crystals of the cerium(IV) complex appear to be stable when dry, unlike the thorium(IV) complex. The ^1H NMR spectrum of the cerium(IV) complex is also similar to that of the thorium(IV) derivative, being exceedingly complicated and indicating the possible presence of two inequivalent *p-tert*-butylcalix[8]arene ligands, for example. Microanalytical results imply that the two complexes differ in composition, and work is in progress to characterise cerium(IV) complexes of *p-tert*-butyl- and other -calix[8]arene ligands in more detail.

Acknowledgements

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