A pentaaluminium complex of calix[6]arene: a bulky ligand that is sterically undemanding

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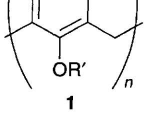
***p-tert*-Butylcalix[6]arene reacts with trimethylaluminium to produce a crystalline pentaaluminium calixarene complex in which an aluminium methyl group resides between two parallel calixarene aromatic rings.**

Although calixarenes (**1**) have attracted intense interest for their potential as organic hosts and selective ionophores,[1] the use of these molecules in their underivatized form as ligands in coordination and organometallic complexes has been largely unexplored. This is despite the varying demonstrations of the ability of calixarenes to act as bulky ligands[2,3] or polyoxo-surfaces[4,5] and the fact that they present the opportunity to design complexes with either hindered open coordination sites[5,6] or ligands encapsulated within a cavity.[7–9] In addition, in common with most calixarene work, the attention to date has been almost exclusively devoted to calix[4]arene (**1**, n = 4) which, while it provides a fairly rigid framework that enables the first two benefits listed above and a cone-shaped cavity that provides the latter two, is a relatively poor example of the full potential of calixarenes. As the number of phenolic rings in a calixarene increases, so does the range of available conformations and, therefore, the number of different potential coordination-sphere geometries and cavity shapes and sizes. With this in mind, we have initiated an investigation of the 'inorganic' chemistry of calix[6]arene (**1**, n = 6),[10] with the hope that the increased flexibility of the molecule will enable greater utilization of the possible benefits mentioned above. In this contribution, we describe the product obtained from the reaction between *p-tert*-butylcalix[6]arene (PTBC, **1**, n = 6, R = Bu^t, R′ = H) and trimethylaluminium.

When neat trimethylaluminium is added to a toluene solution of PTBC, a vigorous reaction occurs accompanied by gas evolution.† Addition of thf to the reaction mixture and slow evaporation results in the growth of highly air-sensitive, solvent-dependent colourless crystals of **2**, suitable for X-ray crystallographic analysis.‡ The structure of **2**, shown in Fig. 1, consists of *p-tert*-butylcalix[6]arene bonded *via* the phenolic oxygens to five aluminium atoms—the highest degree of metallation observed for a calixarene thus far. The calix[6]arene framework adopts a unique conformation in which two opposite aromatic rings are oriented in a fashion that is virtually perpendicular with respect to the average plane of the molecule, while the remaining four rings lie slightly inclined from parallel in the opposite direction. The net result of this alignment is that the six oxygens are virtually coplanar (maximum deviation from plane is 0.2 Å), an arrangement that has been postulated for the binding of UO_2^{2+} by calix[6]arene,[14] but never conclusively demonstrated. The interaction of the aluminium with this hexagonal-planar 'phenoxo-surface' is rather symmetrical. The oxygens of two perpendicular aromatic rings (A and D) each interact with two metal atoms—a terminal aluminium [Al(4) to O(1) and Al(5) to O(4)] which binds to three other moieties [Al(4) is an $AlMe_2$(thf) fragment and Al(5) is a complete $AlMe_3$ unit] and an AlMe fragment that also binds to two other calixarene oxygens [Al(1), which bonds to O(1), O(2) and O(6), and Al(3), which bonds to O(3), O(4) and O(5)]. The Al–O thread is completed by a central $AlMe_2$ fragment [Al(2)] that bridges O(2) and O(3). Charge balance thus dictates that the calixarene acts as a hexaanion. The Al–O bond lengths lie within a fairly wide range of 1.66(1) to 1.944(9) Å, reflecting the difference between true covalent interactions and formal 'donor' bonds.[15] The angles at the aluminium atoms are slightly distorted from tetrahedral, but average between 109.0 and 109.3 ° at each metal centre. It is interesting that, in all cases, the angles associated with the methyl groups are larger than those associated with the calixarene oxygens, implying that the calixarene is not terribly sterically demanding. This conclusion is strengthened by the fact that each aluminium is tetrahedral, despite the rule of thumb that *ortho*-substituted phenoxides in which the substituent is larger than methyl usually enforce the formation of trivalent aluminium monomers.[16]

The unique conformation adopted by the calixarene as a result of 'flexing' to provide a proper coordination environment is such that there is no remaining 'cone-shaped' cavity, as is the case for metal complexes of calix[4]arene. Rather, the aromatic units define a channel in which the 'flattened' rings comprise the base, the perpendicular rings form the sides, and the *tert*-



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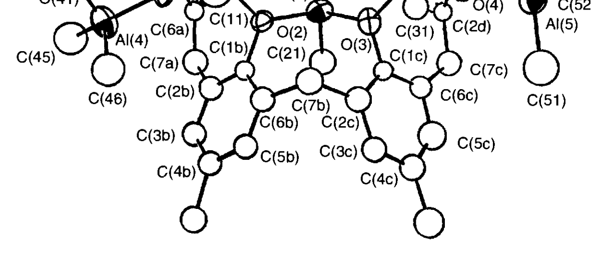

Fig 1 A view of **2** from above the molecule. Methyl carbons of the *tert*- butyl groups and hydrogen atoms are omitted for clarity. Atoms shown with 50% probability ellipsoids. Selected bond lengths: Al(1)–O(1), 1.862(9), Al(1)–O(2) 1.826(9), Al(1)–O(6) 1.67(1), Al(2)–O(2) 1.900(8), Al(2)–O(3) 1.882(9), Al(3)–O(3) 1.862(9), Al(3)–O(4) 1.799(9), Al(3)–O(5) 1.66(1), Al(4)–O(1) 1.828(9), Al(4)–O(41) 1.88(1), Al(5)–O(4) 1.944(9) Å.

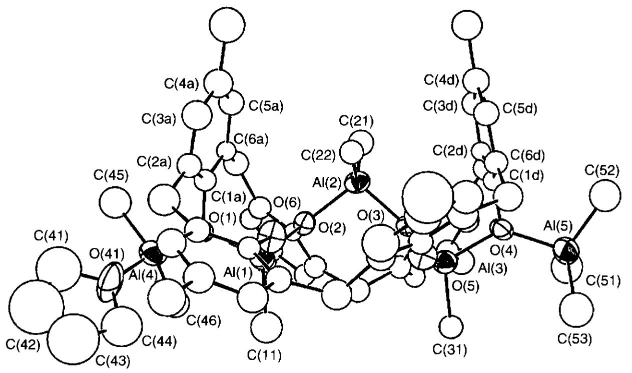

Fig 2 A view of **2** from the side. Methyl carbons of the *tert*-butyl groups and hydrogen atoms are omitted for clarity. Atoms shown with 50% probability ellipsoids.

butyl groups attached to the latter act as a top. This channel is occupied by the two methyl groups attached to Al(2) (Fig. 2), so that C(22) lies in between the two perpendicular aromatics. The C(22)···ring centroid distances are 3.82(1) and 3.64(1) Å, respectively, and the C(22)···C_{ring} distances range from 3.79 to 4.27 Å. The effect of this interaction may be observed in the ^{1}H NMR spectrum, in which one Al–Me resonance is shifted significantly upfield to δ –2.01.

In conclusion, a pentaaluminium complex of calix[6]arene has been isolated in which the calixarene shows sufficient flexibility to adopt a conformation in which both the electronic demands of the metal atoms may be met, yet still retain a cavity in which a metal ligand may be incorporated.

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Footnotes

† *Typical synthetic procedure*: All manipulations were performed under N_2 using standard techniques. To a solution of PTBC (0.49 g 0.50 mmol)[11] in toluene was added dropwise 97% trimethylaluminium (0.20 ml, 2.0 mmol) at room temp. while stirring. After vigorous gas evolution had ceased, the resulting solution was stirred overnight. After addition of thf, and partial evaporation, pure **2** was obtained as a microcrystalline solid (0.28 g, 42.5%). *Spectroscopic data*: **2** ^{1}H (200 MHz) NMR spectrum in C_6D_6: δ –2.01 (s, 3 H), –1.25 (s, 3 H), –1.20 (s, 3 H), –0.94 (s, 3 H), –0.58 (s, 6 H), –0.40 (br s, 9 H), 1.32–1.49 (m, 54 H), 3.22–5.39 (m, 20 H), 7.22 (s, 12 H); ^{27}Al NMR (78 MHz): broad peak at δ 135–150.

‡ *Crystal data* for **2**·2thf·0.5(C_7H_8): $C_{90.5}H_{133}Al_5O_9$, M_w = 1499.97, T = 293 K, triclinic, space group $P\bar{1}$, a = 15.111(4), b = 15.378(3), c = 20.461(4) Å, α = 84.32(2), β = 86.57(2), γ = 88.98(2) °, U = 4722(2) Å^3, Z = 2, $F(000)$ = 1626, D_c = 1.055 g cm^{-3}, μ(Mo-Kα) = 1.04 cm^{-1}. Intensities of 11061 relections ($3 < 2\theta < 44$ °) were measured on an Enraf-Nonius CAD-4 diffractometer using Mo-Kα radiation (graphite monochromator, ω scan mode). Three standard reflections were measured every 3600 second to monitor crystal stability (<5%). Absorption corrections were not applied. The structure was solved by using SHELXS86[12] and refined by full-matrix least squares on F by using MolEN.[13] Due to a paucity of data, only the aluminium and oxygen atoms of the complex were treated with anisotropic thermal parameters, and, where possible, hydrogen atoms were placed in calculated positions and allowed to ride on the attached carbon [3159 reflections with $F > 5\sigma(F)$]. Convergence was reached at R = 0.0730, R_w = 0.0982. Three areas of solvent were included in the model; a toluene molecule that resides on a crystallographic centre of inversion, and two thf molecules (one seriously disordered). The highest peak on the final difference map was 0.39 e Å^{-3}, located near the disordered thf.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No.1.

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