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COMMUNICATION

Synthesis and structure of bis(methylaluminium · $NCCH_3$) *p-tert*-butylcalix[4]arene

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Abstract—Treatment of *p-tert*-butylcalix[4]areneH_4 with $AlMe_3$ in toluene at elevated temperature affords after work-up the complex $\{[MeAl(NCMe)]_2$(*p-tert*-butylcalix[4]arene)}, which adopts a flattened partial cone conformation as characterized by X-ray crystallography. © 1997 Elsevier Science Ltd

Keywords: partial cone conformation; X-ray crystallography; metallocalix[4]arenes.

The metal coordination chemistry of calixarenes is currently enjoying much attention [1]. In particular, metallocalix[4]arenes have been structurally characterized for a number of metals, including Mo [2], W [3], Nb [4] and Ta [4]. These complexes in general retain the cone conformation of the parent ligand, a single metal atom coordinating to all four oxygen atoms. Main-group lower-rim derivatives of calixarenes are still quite rare; examples include phosphates [5(a,b)], phosphinites [5(c,d)] and the double-calixarene structures formed by silicon 5[(e,f)] and aluminium [5(g)]. Here again, the calixarenes retain the cone conformation. In two recent reports [6(a,b)], Raston and coworkers showed that calix[4]arenes can adopt an unusual flattened partial cone conformation. In particular, treatment of *t*-butylcalix[4]arene with excess $AlMe_3$ in toluene gave the fully deprotonated alkylmetal-rich complex {*t*-butylcalix[4]arene$(AlMe)_2$ $(AlMe_3)_2$}. The authors noted that with a 2 : 1 ratio for $AlMe_3$ to the calix[4]arene, ill-defined sparingly soluble powders were formed. This has prompted us to disclose our results, whereupon addition of two equivalents of $AlMe_3$ to *p-tert*-butylcalix[4]arene† followed by extraction of these powders into acetonitrile affords highly crystalline $\{[MeAl(NCMe)]_2$*t*-butylcalix[4]arene} (1).

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† Satisfactory elemental analyses have been obtained.

$AlMe_3$ (2.31 cm^3, 2.0 M solution in toluene, 4.62 mmol) was added to *p-tert*-butylcalix-4-areneH_4 (1.5 g, 2.31 mmol) in toluene (40 cm^3) with rapid stirring. The mixture was heated at 100°C for 12 h. After allowing to cool to room temperature, the volatile components were removed under reduced pressure and the residue was extracted with MeCN (30 cm^3). Prolonged standing (1–2 days) at ambient temperature afforded colourless X-ray quality prisms (0.6 g, 32%).

Selected NMR data for **1**: ^1H NMR (C_6D_6, 298 K): δ 4.88 [d, $^2J_{HH}$ 16 Hz, 4H, ArCH_2Ar], 3.63 [d, $^2J_{HH}$ 16 Hz, 4H, ArCH_2Ar], -1.21 [s, Al-CH_3].

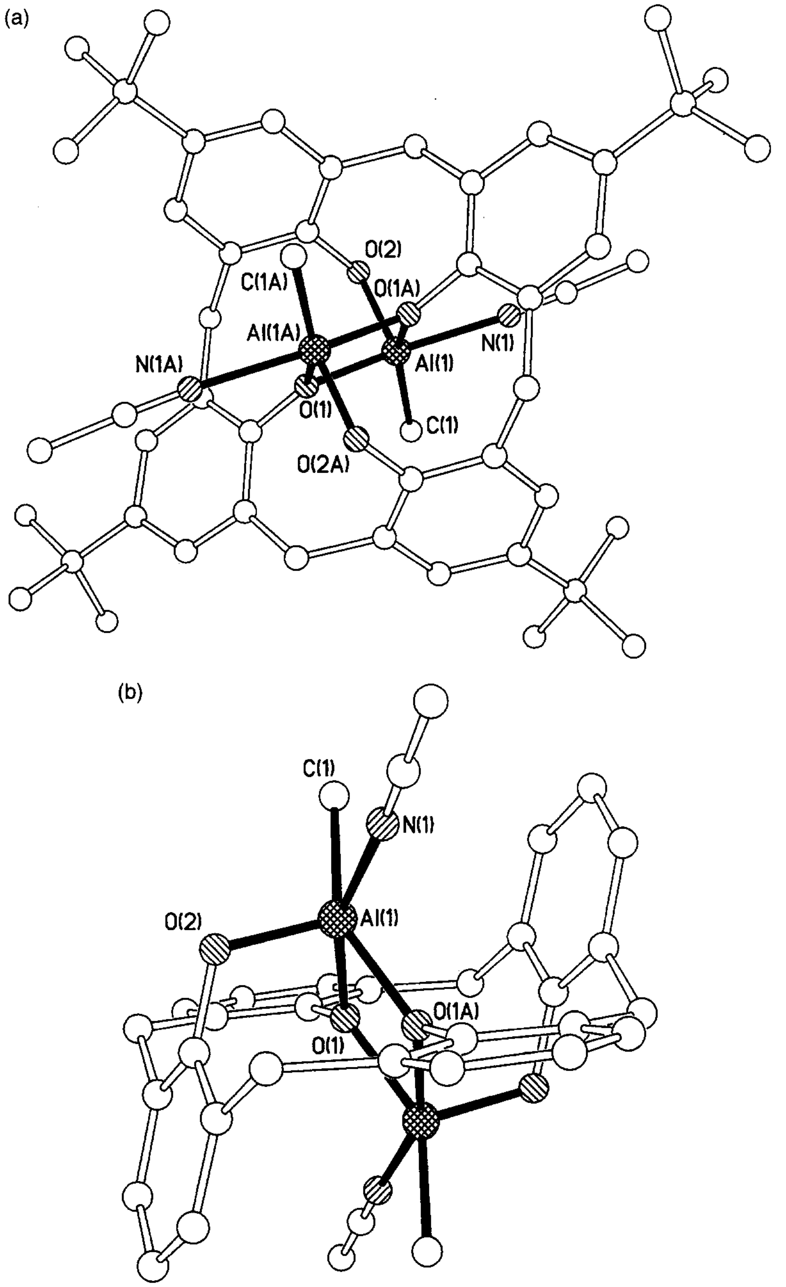

Fig. 1. Views of the molecular structure of **1** (a) through the calixarene ring showing the Al_2O_2 core and (b) showing the flattened partial cone conformation. Selected dimensions (Å and °) : Al(1)—O(1) 1.9192(9), Al(1)—O(1A) 1.8540(9), Al(1)—O(2) 1.7616(9), Al(1)—C(1) 1.9512(14), Al(1)—N(1) 2.1291(12); O(1)—Al(1)—N(1) 158.75(5), C(1)—Al(1)—O(2) 111.57(5), C(1)—Al(1)—O(1A) 147.20(5), O(2)—Al(1)—O(1A) 101.18(4), O(1)—Al(1)—O(1A) 74.35(4), Al(1)—O(1)—Al(1A) 105.65(4). Atoms with suffix A are symmetry related by inversion to corresponding atoms without the suffix. In 1(b) the *p*-*tert*-butyl groups have been removed for clarity.

Crystals of **1** suitable for an X-ray determination[‡] were grown from acetonitrile at $-20°C$; they incorporate two additional uncoordinated molecules of solvent per molecule of the complex. Two views of the molecular structure are shown in Fig. 1 and reveal the partially flattened double cone conformation with idealized C_{2v} symmetry. The aluminium centres are distorted trigonal bipyramidal (as expected for three 'single' and two dative covalent bonds to 5-coordinate Al) [7] with two oxygen atoms [O(1A) and O(2) for Al(1)] and a methyl group [C(1)] forming the trigonal plane; acetonitrile [N(1)] and the third oxygen atom [O(1)] occupy the apical positions. The Al—O bond lengths vary significantly; Al(1)—O(2) [1.7616(9)Å] is in the range normally found for terminal aluminium phenolates [1.640(5)–1.773(2)Å] [8], whereas Al(1)—O(1A) [1.8540(9)Å] and the longest bond Al(1)—O(1) [1.9192(9)Å] are bridging. The binuclear monomeric nature of **1** provides an interesting contrast to the aluminium-fused double-calix-4-arene structure noted earlier [5(g)], and is doubtless due to the absence of any H-bonding interactions in **1**. Both structures, however, do contain a central Al_2O_2 four-membered ring system. Two bulky aryloxides of aluminium, namely $[AlR(OAr)_2]$ (R = Me, ^{t}Bu; OAr is derived from 2,6-di-*tert*-butyl-4-methylphenol, or an analogue thereof), have been found to adopt an unusual coplanarity of the two phenoxide rings perpendicular to the AlO_2 plane [9(a,b)]. Figure 1 (a) reveals that **1** can be viewed in a similar manner with the rings associated with O(1) and O(1a) forming the plane almost perpendicular to the Al_2O_2 core.

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[‡] *X-ray crystallography*

Crystal data for **1**. 2MeCN: $C_{50}H_{64}Al_2N_2O_4 \cdot 2CH_3CN$, $M = 893.1$, triclinic, space group $P\bar{1}$, $a = 9.0316(7)$, $b = 12.2766(9)$, $c = 12.6541(10)$Å, $\alpha = 73.235(2)$, $\beta = 74.090(2)$, $\gamma = 72.612(2)°$, $V = 1254.6(2)$Å^3, $Z = 1$, $D_c = 1.182$ gcm^{-3}, $\mu = 0.11$ mm^{-1} (Mo-Kα, $\lambda = 0.71073$Å), $T = 160$ K. 8121 reflections were measured on a Siemens SMART CCD area-detector diffractometer and corrected semiempirically for absorption (transmission 0.874–0.934), yielding 5470 unique data ($2\theta_{max} = 57.0°$, $R_{int} = 0.0199$). The structure was determined by direct methods and refined by F^2 for all data, with anisotropic displacement parameters, and riding isotropic H atoms. Final $R_w = \{\Sigma[w(F_o^2 - F_o^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1005$ for all data, conventional $R = 0.0369$ on F values of 4786 reflections with $F_o^2 > 2\sigma(F_o^2)$; goodness of fit = 1.082 for all F^2 values and 299 refined parameters. All final difference map features were within ± 0.3 eÅ^{-3}. Programs: Siemens SMART (control), SAINT (integration) and SHELXTL, and local programs. Atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre.