Multinuclear metallocalix[4]arenes incorporating ethylzinc groups

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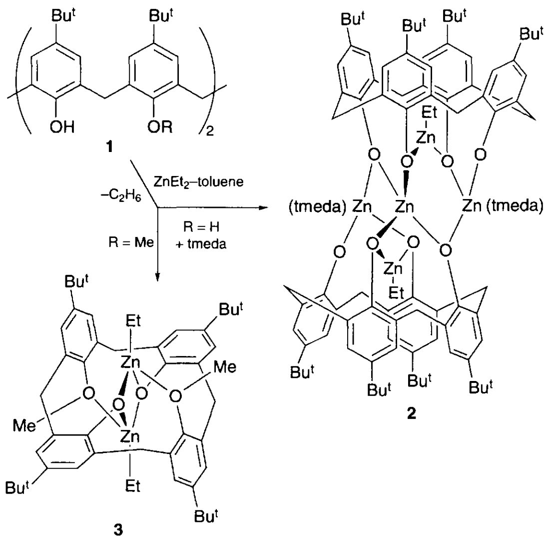
Reaction of *p*-Bu^t-calix[4]arene (H_4L) with excess $ZnEt_2$ (tmeda) in toluene affords the fully deprotonated, bis-calixarene complex, [$Zn_5L_2Et_2(tmeda)_2$], with each ethyl group *endo* to a calixarene in the cone conformation; reaction of 1,3-dimethyl ether *p*-Bu^t-calix[4]arene (H_2L) with $ZnEt_2$ yields the mono-calixarene complex [$Zn_2L'Et_2$], the calixarene adopting a doubly flattened partial cone conformation.

A feature of the metal-ion chemistry of the ubiquitous Bu^t-calix[4]arene (H_4L) is its ability to form molecular assemblies based on linking two calixarenes *via* complexation involving the O centres, notably for Al^{III},[1] Si^{IV},[2] Ti^{IV},[3] Nb^{V},[4] Eu^{III}[5] and Zn^{II}.[6] In these complexes the calixarene is versatile in acting as a poly-phenolate or a mixed poly-phenolic/phenolate ligand, in so doing retaining a cone conformation of some note which is capable of acting as a receptor. Mono-calixarene species are also accessible for *p*-Bu^t-calix[4]arene,[7] and for calix[4]arene (H_4L''), for example in reaction with MMe_3 (M = Al, Ga) which yields the metal-rich species, [$(MMe)_2L''(MMe_3)_2$], with a thread of metal centres passing through the annulus of the molecule.[8] However, mono- calixarene complexes appear to be more readily accessible using partially O-alkylated *p*-Bu^t-calix[4]arene. This includes Zr^{IV}[9] and Al^{III}[8,10] complexes of 1,3-dimethyl ether *p*-Bu^t-calix[4]arene (H_2L'; R = Me, **1**, Scheme 1) and an Na^+ complex of O-permethylated *p*-Bu^t-calix[4]arene.[11]

An earlier study on the reaction of Bu^t-calix[4]arene with 2 equiv. of $ZnEt_2$ yielded a divergent bis-calixarene species based on two metal centres, [$Zn_2(H_2L)$], with a methylene chloride in each cavity.[6] This complex has residual phenolic protons, two of which are uncoordinated and offer scope for building up larger clusters of metal centres. Indeed, we now show that the use of excess $ZnEt_2$ in the presence of tmeda (*N,N,N′,N′*-tetramethylethylenediamine) yields a new class of bis-metallocalixarene complex based on five metal centres showing three different coordination environments. Three metal centres link the O-rims of the calixarenes, the other two are novel in bearing an ethyl group which is *endo* to the cavity of a calixarene. We also show that treatment of 1,3-dimethyl ether *p*-Bu^t-calix[4]arene with $ZnEt_2$ yields a monocalixarene species involving two metal centres, with the calixarene in a partially flattened double cone conformation. These ethylzinc containing complexes have implications in catalytic alkylation reactions,[12] and the pentanuclear complex is noteworthy in the use of calixarenes to build up large metal clusters.



Scheme 1

Treatment of H_4L (R = H, **1**) with an excess of $ZnEt_2$ (tmeda) in toluene resulted in a vigorous exothermic reaction accompanied by gas evolution with the reaction mixture affording colourless, air-sensitive crystals of [$Zn_5L_2Et_2(tmeda)_2$] **2**, and treatment of H_2L' with $ZnEt_2$ similarly removes all available phenolic protons affording [$Zn_2L'Et_2$], **3**, Scheme 1.‡ Compounds **2** and **3** were characterised using ^1H and ^{13}C NMR spectroscopy, and X-ray diffraction.

In the solid state, molecules of **2** have crystallographically imposed C_2 symmetry with the symmetry axis passing through the central metal centre, and normal to the principal axis of each of the calixarene cavities, Fig. 1. The two calixarenes are fused by three of the five zinc centres. One of these is the central zinc which is coordinated by two oxygen atoms from each calixarene unit thereby achieving a four-fold coordination environment. The other two metal centres connecting the calixarenes are five coordinate, bound by one oxygen atom on one calixarene, two adjacent oxygen atoms on the other calixarene unit and a molecule of tmeda. The ethyl groups are located *endo* relative to the cone of the calixarenes with the associated trigonal-planar zinc centres also bound by two oxygen centres from opposite aromatic rings in the same calixarene. This type of coordination environment has precedence in alkyloxo–organozinc chemistry,[13] and a related metal-bound *endo* hydrido group is found in [AlL′H].[10] Four-coordinate centres are found in [$Zn_2(H_2L)_2$],[6] albeit with a phenolic O centre attached to each metal centre, and the presence of a central Zn_2O_2 core like that found in the solid state of **3**. The dihedral angles between pairs of opposite phenyl groups in each calixarene are significantly different with the more acute angle associated with those not bound to the organozinc moiety, 29.1(3), *cf.* 70.0(3) for the other pair. These values compare with 59 and 70° for [$Zn_2(H_2L)_2$],[6] reflecting a more flattened cone in this compound.

Molecules of **3** (Fig. 2) are centrosymmetric with distorted tetrahedral metal centres as part of a planar Zn_2O_2 core involving the two phenolate O centres. The other ligands attached to each metal centre are a residual ethyl group and an O centre bearing a methyl group. In the related Al and Ga compounds, [$(MMe)_2(MMe_3)_2L$] (M = Al, Ga[8]), the latter are phenolate O centres which bind to terminal MMe_3 groups. The calixarene adopts the doubly flattened partial cone conformation which is not conducive to the formation of molecular inclusion complexes. Two opposite aromatic rings are co-planar with the other two intersecting the ‘flattened’ plane with

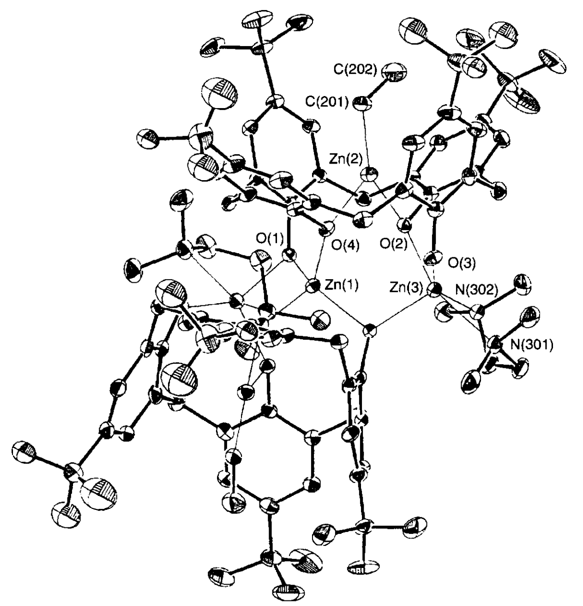


Fig. 1 Molecular projection of **2** (20% ellipsoids); selected distances (Å) and angles (°): Zn(1)–O(1,4) 1.971(5), 1.954(5), Zn(2)–O(2,4) 2.040(5), 1.971(5), Zn(2)–C(201) 1.955(8), Zn(3)–O(2,3) 2.094(5), 1.932(5), Zn(3)–N(301,302) 2.370(8), 2.213(7), Zn(3)–O(1′) 2.073(4), O(1)–Zn(1)–O(4,1′,4′) 103.9(2), 119.0(2), 110.7(2), O(2)– Zn(1)–O(4) 88.6(2), O(2,4)–Zn(2)–C(201) 138.5(3), 131.1(3), O(2)– Zn(3)–O(3), N(301,302), O(1′) 90.1(2), 159.0(2), 94.6(2), 93.9(2), O(3)–Zn(3)–N(301,302), O(1′) 87.3(2), 149.0(2), 109.3(2), N(301)– Zn(3)–N(302), O(1′) 77.4(3), 106.7(2), N(302)–Zn(3)–O(1′) 100.9(2), Zn–O(1)–Zn(3′) 108.9(2), Zn(2)–O(2)–Zn(3) 119.9(2), Zn(1)–O(4)–Zn(2) 118.8(2), Zn(1)···Zn(2,3) 3.379(1), 3.290(1), Zn(2)···Zn(3) 3.579(2)

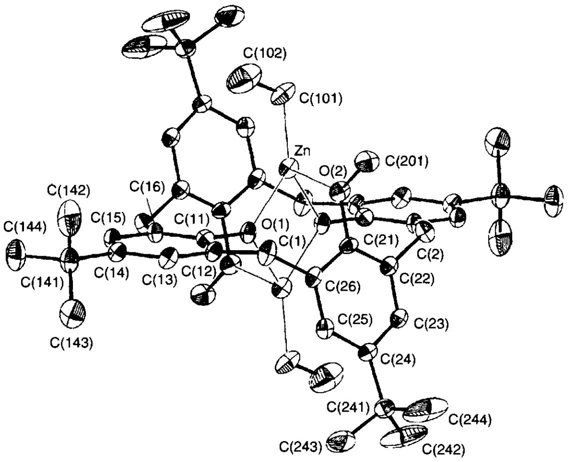


Fig. 2 Molecular projection of **3** (20% ellipsoids); selected distances (Å) and angles (°): Zn–O(1,2,1′), C(101), 1.957(4), 2.222(7), 1.984(5), 1.930(9), O(1)–Zn–O(2,1′), C(101), 86.6(2), 74.9(2), 138.3(3), O(2)–Zn–O(1′), C(101) 88.5(2), 101.7(4), O(1′)–Zn–C(101) 144.6(4), Zn–O(1)–Zn′ 105.1(2), Zn···Zn 3.143(2)

dihedral angles of 111.1(4)°, *cf.* 109–115° for [(MMe)$_2$(M-Me$_3$)$_2$L].[8] The individual geometries of the metal centres in **2** and **3** are unexceptional.[14]

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Footnotes

† *Synthesis*: [Zn$_5$L$_2$Et$_2$(tmeda)$_2$] **2**; *p*-Bu^t-calix[4]arene (1.00 g, 1.54 mmol) was slowly added to a solution of ZnEt$_2$(tmeda) (1.20 g, 5.01 mmol) in toluene (70 ml) at 0 °C. Gas evolution was observed and the solution was allowed to warm to room temperature. After standing for several weeks at room temperature an initially formed solid dissolved and after concentrating *in vacuo* colourless crystals deposited over two days, yield 1.26 g, 86%, mp 110 °C (decomp.); ^{1}H NMR (200 MHz, C$_6$D$_6$, 25 °C) δ −2.00 (4 H, m, ZnCH$_2$), −0.37 (6 H, t $^3J_{HH}$ 8 Hz, CH$_2$C*H*$_3$), 1.03 (18 H, s, CMe$_3$), 1.27 (18 H, s, CMe$_3$), 1.31 (18 H, s, CMe$_3$), 1.39 (18 H, s, CMe$_3$), 1.94 (8 H, s, NCH$_2$), 2.06 (24 H, s, NCH$_3$), 3.25 (2 H, d $^2J_{HH}$ 13 Hz, CH$_2$), 3.41 (2 H, d $^2J_{HH}$ 12 Hz, CH$_2$), 3.50 (2 H, d $^2J_{HH}$ 14 Hz, CH$_2$), 3.65 (2 H, d $^2J_{HH}$ 15 Hz, CH$_2$), 4.15 (2 H, d $^2J_{HH}$ 14 Hz, CH$_2$), 5.25 (2 H, d $^2J_{HH}$ 13 Hz, CH$_2$), 5.34 (2 H, d $^2J_{HH}$ 12 Hz, CH$_2$), 6.48 (2 H, d $^2J_{HH}$ 14 Hz, CH$_2$), 6.83–7.41 (16 H, m, CH); ^{13}C NMR (200 MHz, C$_6$D$_6$, 25 °C) δ −10.2 (ZnCH$_2$), 12.4 (CH$_2$*C*H$_3$), 31.1, 31.5, 31.8, 31.9 (C*Me*$_3$), 33.6, 33.7, 33.7, 33.9 (CH$_2$), 36.4, 36.4, 36.8, 36.8 (*C*Me$_3$), 47.8 (NMe), 57.6 (NCH$_2$), 121.7, 125.3, 125.6, 125.7, 125.8, 126.0, 127.0, 127.1, 128.1, 128.5, 129.6, 131.1, 131.7, 131.8, 132.9, 137.5, 137.6, 140.9, 141.7, 142.2, 156.4, 156.8, 158.0, 158.1 (CH) (Found: C, 65.41; H, 7.85; N 3.36. Calc. for C$_{104}$H$_{146}$O$_8$N$_4$Zn$_5$: C 65.50, H 7.72, N 2.94%).

[Zn$_2$L′Et$_2$], **3**; to 1,3-dimethyl ether *p*-Bu^t-calix[4]arene (0.25 g, 0.37 mmol) in toluene (20 ml) at 0 °C was slowly added neat ZnEt$_2$ (0.10 g, 0.81 mmol). After 12 h the solution was concentrated *in vacuo* and on cooling to −30 °C colourless crystals formed, yield 0.20 g, 64%, mp 270 °C (decomp.); ^{1}H NMR (200 MHz, C$_6$D$_6$, 25 °C) δ −0.21 (4H, q $^3J_{HH}$ 8 Hz, ZnCH$_2$), 0.92 (6 H, t $^3J_{HH}$ 8 Hz, CH$_2$C*H*$_3$), 1.27 (1 8H, s, CMe$_3$), 1.39 (18 H, s, CMe$_3$), 3.25 (6 H, s, OMe), 3.59 (4 H, d $^2J_{HH}$ 15 Hz, CH$_2$), 4.22 (4 H, d $^2J_{HH}$ 15 Hz, CH$_2$), 7.01 (4 H, s, CH), 7.35 (4 H, s, CH); ^{13}C NMR (200 MHz, C$_6$D$_6$, 25 °C) δ −8.3 (ZnCH$_2$), 12.1 (CH$_2$*C*H$_3$), 31.6, 32.1 (C*Me*$_3$), 34.2, 34.8 (*C*Me$_3$), 35.6 (CH$_2$), 59.8 (OMe), 126.1, 126.8, 129.6, 133.9, 140.7, 148.3, 153.9, 158.6 (CH) (Found: C, 68.91; H, 7.83. Calc. for C$_{50}$H$_{68}$O$_4$Zn$_2$: C 69.52, H 7.93%).

‡ *Crystal structure determinations*: (CAD4 diffractometer, crystals mounted in capillaries). **2**·4C$_7$H$_8$: C$_{132}$H$_{178}$N$_4$O$_8$Zn$_4$, monoclinic, *C*2/*c* (no. 15), a = 30.953(6), b = 14.596(5), c = 28.49(2) Å, β = 102.08(3),U = 12586(9) Å^3, D_c = 1.201, μ = 9.9 cm^{-1}, $A^*_{min,max}$ = 1.21, 1.33 (gaussian correction), Z = 4, Mo-Kα radiation, 11 073 unique reflections, $2\theta \leqslant 50°$ [5756 observed, $I > 3.0\sigma(I)$], T = 297 K, R = 0.062, R' = 0.068. **3**·2C$_7$H$_8$: C$_{64}$H$_{84}$O$_4$Zn$_2$, triclinic, $P\bar{1}$ (no. 2) a = 12.742(3), b = 12.394(6), c = 10.919(2) Å, α = 66.52(3), β = 76.23(2), γ = 67.06(3), U = 1449.6(9) Å^3, D_c = 1.201, μ = 8.7 cm^{-1}, $A^*_{min,max}$ = 1.13, 1.18, Z = 1, Mo-Kα radiation, 3780 unique reflections, $2\theta \leqslant 45°$ [1985 observed, $I > 3\sigma(I)$], T = 297 K, R = 0.054, R' = 0.053. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/230.

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