Binuclear tin and germanium calix[4]arenes

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Ditin(II) and digermanium(II) calix[4]arenes, [Bu^{t}calix]M$_2$ (1, M = Sn; 2, M = Ge) have been prepared by treatment of [Bu^{t}calix]H$_4$ with M(NR$_2$) (R = Me or Me$_3$Si); the reaction of [Bu^{t}calix]Li$_4$ with SnCl$_4$ affords the mixed valence ditin derivative [Bu^{t}calix]Sn$_2$Cl$_2$ 3.

Calixarenes offer the prospect of serving as oxo-matrices for the construction of poly-Lewis acid or poly-Lewis base assemblies. Although there is considerable current interest in this field,[1] relatively little information is available regarding main group calixarene chemistry, particularly for systems that feature more than one main group element in the lower rim. Such polyfunctionalized derivatives are limited to alkali metals,[2] aluminium,[3] gallium,[3c] silicon,[4] and phosphorus.[2,4a,5,6] We report the synthesis and X-ray crystal structures of (i) the first binuclear tin(II) calixarene, (ii) the first binuclear germanium(II) calixarene, and (iii) a calixarene that features both a tin(II) and a tin(IV) centre.[7]

The reaction of [Bu^{t}calix]H$_4$ with Sn(NMe$_2$)$_2$ took place in toluene solution at ambient temperature and afforded a 78% yield of colorless, crystalline [Bu^{t}calix]Sn$_2$ **1**.† The HRMS (CI) for **1** exhibited a parent peak corresponding to the composition C$_{44}$H$_{52}$O$_4$Sn$_2$ and an isotopic distribution consistent with the presence of two tin atoms. The ^{1}H NMR spectrum of **1** revealed the presence of two pairs of *para*-Bu^{t}ArO moieties and the ^{119}Sn NMR spectrum consisted of a single peak at δ 23.0. Further characterisation necessitated an X-ray crystal structure determination.‡ The solid state (Fig. 1) consists of individual molecules of **1** and CH$_2$Cl$_2$; there are no unusually short intermolecular contacts. The central structural feature of **1**, which resides on a centre of symmetry, is an Sn$_2$O$_2$ parallelogram. The bond angles at tin [68.2(1)°] and oxygen [111.8(1)°] within the Sn$_2$O$_2$ kernel deviate significantly from 90° and the two Sn–O bonds differ in length by *ca.* 0.2 Å. Each tin atom is bonded to a third oxygen and this bond distance [Sn(1)–O(2)] is *ca.* 0.1 Å shorter than those in the Sn$_2$O$_2$ parallelogram. The O–Sn–O bond angles of the SnO$_3$ moiety are remarkably acute as shown in the graphical abstract (sum of O–Sn–O bond angles = 240.02°). The structure of **1** can be considered to arise *via* the dimerisation of two otherwise coordinatively unsaturated (ArO)$_2$Sn units as shown below (**A**). As a consequence of the formation of two donor–acceptor bonds, the conformation of the calix[4]arene changes from bowl-shaped to that of a flattened partial cone (**B**).

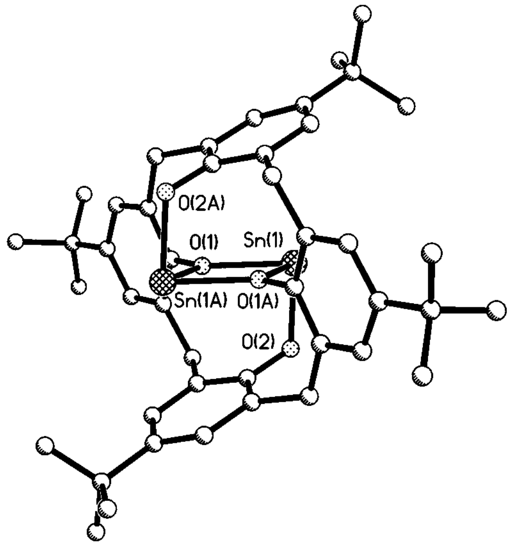
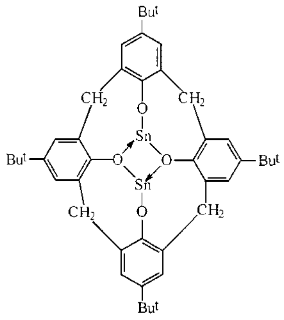
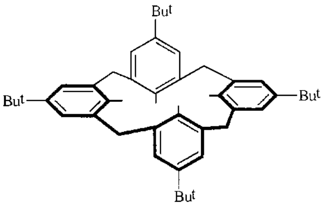


Fig. 1 Molecular structure of **1** showing the atom numbering scheme. Selected bond distances (Å) and angles (°) for **1** (the corresponding values for **2** are shown in parentheses) Sn(1)–O(1) 2.193(2) [Ge(1)–O(1) 1.997(6)], Sn(1)–O(1A) 2.169(2) [Ge(1)–O(1A) 1.991(6)], Sn(1)–O(2) 2.054(2) [Ge(1)–O(2) 1.844(6)]; O(1)–Sn(1)–O(1A) 68.22(11) [O(1)–Ge(1)–O(1A) 71.9(2)], Sn(1)–O(1)–Sn(1A) 117.78(11) [Ge(1)–O(1)–Ge(1A) 108.1(2)], O(1)–Sn(1)–O(2) 86.02(9) [O(1)–Ge(1)–O(2) 91.0(3)], O(2)–Sn(1)–O(1A) 85.78(9) [O(2)–Ge(1)–O(1A) 92.2(2)]. Because there are two half molecules in the asymmetric unit, there are two independent molecules for both **1** and **2**. The metrical parameters for these pairs of independent molecules do not differ greatly and only one such molecule is shown in either case.



A



B

The digermanium derivative [Bu^{t}calix]Ge$_2$ **2** was prepared in an analogous fashion† in 26% yield by treatment of [Bu^{t}calix]H$_4$ with Ge[N(SiMe$_3$)$_2$]$_2$. The virtually identical ^{1}H NMR data for **1** and **2** implied similar structures for both compounds. Confirmation was provided by X-ray analysis (Fig. 1).‡ Comparable trends are evident in the metrical parameters for **1** and **2**, namely within the central Ge$_2$O$_2$ moiety the bond angle at germanium [71.9(2)°] is smaller than that at oxygen [108.1(2)°] and the bond distance of the exterior oxygen [O(2)] is shorter than those within the ring. However, in the case of **2**, the intra-annular bond distances are the same within experimental error.

The reaction of [Bu^{t}calix]Li$_4$ with SnCl$_4$ in diethyl ether solution afforded a ditin derivative of composition [Bu^{t}calix]Sn$_2$Cl$_2$ **3** in 45% yield.† The observation of two peaks in the ^{119}Sn NMR spectrum† indicated that the tin atoms are present in distinctly different environments. By means of X-ray crystallography,‡ it was established that the molecular structure involves a flattened cone or boat-type conformation in which the tin atoms occupy *exo* and *endo* positions (Fig. 2). The hexacoordinate *exo* tin atom adopts a distorted octahedral geometry, being bonded to O(1), O(2), O(3), O(4), Cl(1) and Cl(2). Two of these interactions, O(1) and O(3), can be regarded as donor–acceptor bonds hence Sn(1) is in the +4 oxidation state. As expected, the Sn(1)–O(1) and Sn(1)–O(3) bond distances [av. 2.126(6) Å] are longer than the Sn(1)–O(2) or

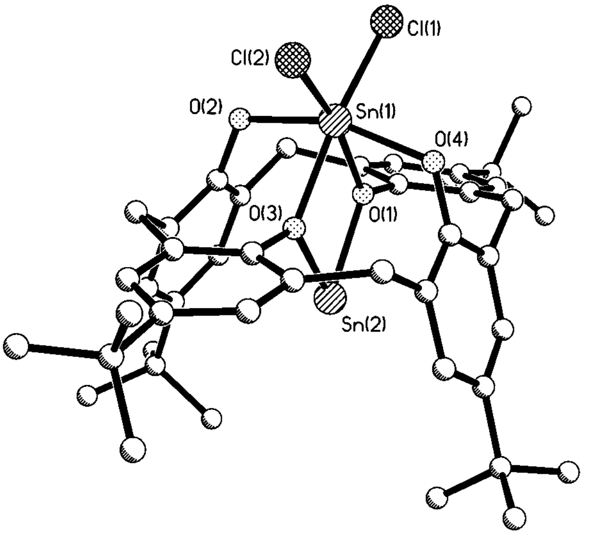


Fig. 2 Molecular structure of **3** showing the atom numbering scheme. Selected bond distances (Å) and angles (°): Sn(1)–Cl(1) 2.340(3), Sn(1)–Cl(2) 2.349(3), Sn(1)–O(1) 2.124(6), Sn(2)–O(1) 2.118(6), Sn(2)–O(3) 2.089(6), Sn(1)–O(3) 2.128(6), Sn(1)–O(2) 2.044(7), Sn(1)–O(4) 2.079(7); Cl(1)–Sn(1)–Cl(2) 100.7(1), O(1)–Sn(1)–O(3) 72.0(2), Sn(1)–O(1)–Sn(2) 107.0(3), O(1)–Sn(2)–O(3) 72.9(2), Sn(2)–O(3)–Sn(1) 107.9(3), O(2)–Sn(1)–O(4) 160.1(3).

Sn(1)–O(4) distances [av. 2.061(7) Å]. There is considerable departure from the ideal octahedral angles at Sn(1) due to the demands of the ligand system. Thus the angles O(2)–Sn(1)–O(4) [160.1(3)°] and O(1)–Sn(1)–O(3) [72.0(2)°] are unusually small whilst the Cl(1)–Sn(1)–Cl(2) bond angle is enlarged commensurately [100.7(1)°]. The *endo* tin atom, Sn(2), is two-coordinate and thus in the +2 oxidation state. The Sn(2) geometry is V-shaped with an O(1)–Sn(2)–O(3) bond angle of 72.9(2)°.

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Notes and references

† *Experimental procedures*: **1**: a solution of 4.2 mmol (0.87 g) of $Sn(NMe_2)_2$ in 30 mL of toluene was added *via* cannula to a toluene suspension of 2.1 mmol (1.37 g) of *p-tert*-butylcalix[4]arene at room temperature. Following the complete addition of $Sn(NMe_2)_2$, the solution turned clear and, after 15 min, a white precipitate formed. The reaction mixture was allowed to stir overnight and the toluene was removed *in vacuo*. The remaining white solid was washed with hexane (3 × 50 mL) and redissolved in 60 mL of CH_2Cl_2. The solution was filtered and stored for two days at −20 °C resulting in the formation of colorless X-ray quality crystals (1.45 g, 78% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (s, 4H, Ar), 7.19 (s, 4H, Ar), 4.46 (d, 4H, CH_2), 3.64 (d, 4H, CH_2), 1.40 (s, 18H, Bu^t), 1.25 (s, 18H, Bu^t); MS (CI) *m/z* (M^+) 877; HRMS (CI) *m/z* calc. for $C_{44}H_{53}O_4Sn_2$: 877.197873, found 877.196806 (M^+).

2: this colorless, crystalline compound was prepared in 26% yield using the procedure described for **1**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (s, 4H, Ar), 7.20 (s, 4H, Ar), 4.45 (d, 4H, CH_2), 3.63 (d, 4H, CH_2), 1.40 (s, 18H, Bu^t), 1.26 (s, 18H, Bu^t); MS (CI) *m/z* (M^+) 789; HRMS (CI) *m/z* calc. for $C_{44}H_{53}O_4Ge_2$: 785.242885, found 785.242345.

3: A diethyl ether solution of 4.0 mmol (2.50 g) of *p-tert*-butylcalix[4]arene was treated with a 1.6 M solution of *n*-BuLi (16.0 mmol, 10.0 mL) at room temperature and the resulting orange slurry and was stirred for 2 h. Neat $SnCl_4$ (0.5 mL, 4.0 mmol) was added *via* syringe to the suspension whereupon the colour changed from orange to dark red. The reaction mixture was allowed to stir overnight, following which the solvent and volatiles were removed *in vacuo*. The residual red solid was redissolved in 50 mL of toluene. The solution was filtered and stored for two weeks at −20 °C resulting in the formation of colorless X-ray quality crystals (1.68 g, 45% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (s, 4H, Ar), 7.26 (s, 4H, Ar), 4.47 (d, 4H, CH_2), 3.61 (d, 4H, CH_2), 1.49 (s, 18H, Bu^t), 1.19 (s, 18H, Bu^t); ^{119}SnNMR (111.85 MHz, $CDCl_3$) δ 215.5, −51.6; MS (CI) *m/z* (M^+) 877; HRMS (CI) *m/z* calc. for $C_{44}H_{52}Cl_2O_4Sn_2$: 946.127753, found 946.127928 (M^+).

‡ *Crystal data*: **1**: $C_{44}H_{52}O_4Sn_2 \cdot 2CH_2Cl_2$, $M = 1052.09$, triclinic, space group $P\bar{1}$, $a = 12.903(2)$, $b = 14.1920(10)$, $c = 14.236(2)$ Å, $\alpha = 91.72(1)$, $\beta = 109.35(1)$, $\gamma = 111.12(1)°$, $U = 2261.1(5)$ Å^3, $Z = 2$, $D_c = 1.545$ g cm^{-3}, $T = 163(2)$ K, $\mu = 1.382$ mm^{-1}, $wR_2 = 0.0983$ (8997 independent reflections), $R = 0.0351$ [$I > 2\sigma(I)$]. There is residual electron density near the tin atom.

2: $C_{44}H_{52}Ge_2O_4 \cdot 3.5CH_2Cl_2$, $M = 1087.28$, triclinic, space group $P\bar{1}$, $a = 13.201(2)$, $b = 14.188(2)$, $c = 15.212(2)$ Å; $\alpha = 84.63(1)$, $\beta = 73.46(1)$, $\gamma = 64.98(1)°$, $U = 2473.8(6)$ Å^3, $Z = 2$, $D_c = 1.460$ g cm^{-1}, $T = 183(2)$ K, $\mu = 1.635$ mm^{-1}, $wR_2 = 0.2629$ (9687 independent reflections), $R = 0.0860$ [$I > 2\sigma(I)$].

3: $C_{44}H_{52}Cl_2O_4Sn_2 \cdot 2.5C_7H_8$, $M = 1183.47$, monoclinic, space group $P2_1/c$, $a = 19.286(4)$, $b = 12.008(2)$, $c = 23.956(4)$ Å, $\beta = 96.26(2)°$, $U = 5515(2)$ Å^3, $Z = 4$, $D_c = 1.425$ g cm^{-3}, $T = 183(2)$ K, $\mu = 1.049$ mm^{-1}, $wR_2 = 0.2666$ (8717 independent reflections), $R = 0.0981$ [$I > 2\sigma(I)$]. CCDC 182/1091. See http://www.rsc.org/suppdata/cc/1999/17/ for crystallographic files in cif format.

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