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Synthesis and X-ray crystal structures of the first antimony and bismuth calixarene complexes†

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The reaction of the monosodium salt of *p-tert*-butylcalix[4]arene (Bu^{t}C4) with 2 equivalents of $SbCl_3$ provides Bu^{t}C4$(SbCl)_2$ and the first bismuth calixarene complex was prepared by treatment of *p-tert*-butylcalix[8]arene (Bu^{t}C8) with $Bi[N(SiMe_3)_2]_3$ in toluene.

Calixarenes provide unique platforms for both mono- and polymetallic assemblies.[1] Their potential applications include homogeneous catalysis and model systems, supramolecular chemistry, materials precursors, ion complexation and/or transport agents, and many other areas.[2] Although there is considerable current interest in this field, main group metallocalixarenes are sparse in comparison to transition and f-block metallocalixarenes.[3,4] Metal aryloxides in general are found in metalloproteins, organometallic catalysts, and complexing agents,[5] while the metal–π interactions often found in the heavier congeners have interesting implications in areas such as ion recognition and biological transport.[6,7] However, the dearth of information on the aryloxide chemistry of the heavy main group elements antimony(III) and bismuth(III) has been noted in recent years.[8,9]

Recently we reported the synthesis and characterization of mono- and dianions of calixarenes as potential precursors for metal complexes.[6,10] Herein we report the synthesis and X-ray crystal structures of the first antimony(III) calix[4]arene (using the monoanion of **Bu^{t}C4** as precursor) and bismuth(III) complex of **Bu^{t}C8**. The antimony complex provides a reactive Sb–Cl bond that will be used to study the effects of this novel ligand environment on the Sb center. The metal-rich Bi(III) calix[8]arene complex is an intriguing structure in which a main group metal cluster is supported and enveloped by organic calixarene and π-bound toluene ligands.

The reaction of the monosodium salt of **Bu^{t}C4** with 2 equivalents of $SbCl_3$ was carried out in THF solution at ambient temperature and afforded a 69% yield of white powder (**Bu^{t}C4**$(SbCl)_2$) **1**. When 1 equivalent of $SbCl_3$ was used the yield of **1** was 29%, and excess **Bu^{t}C4** was recovered. Single crystals were obtained by recrystallization of **1** from THF solution at −35 °C or slow evaporation of solvent. The solubility of **1** is poor in most organic solvents. The ^1H NMR spectrum of **1** in THF shows two pairs of doublets for the methylene groups (4.45, 4.36, 3.74, and 3.39 ppm), two doublets for the aromatic protons (7.21 and 7.12 ppm), and two singlets for the *tert*-butyl groups (1.35 and 1.26 ppm).

The X-ray crystal structure of **1**·4(THF) was determined (Fig. 1).‡ The core structural feature of **1** is a centrosymmetrical $Sb_2(\mu\text{-}O)_2$ parallelogram with *trans* Cl atoms. This structural feature of **1** is quite similar to the Sn_2O_2 core of the Sn(II) calix[4]arene complex reported by McBurnett and Cowley.[3] The Sb(1)–O(1) and Sb(1)–O(1A) distances in the cycle are quite different, 2.457(2) and 2.027(2) Å, respectively. The Sb–O(THF) distance, 2.631(2) Å, indicates that the O atom of the THF molecule is also involved in coordination of the Sb atom. Thus, coordination of the Sb atom in **1** can be described as a distorted pyramid with the O(1), O(1A), Cl(1), and O(3) fragment planar within 0.04 Å. The apical Sb(1)–O(2) distance, 1.988(2) Å, is close to the short Sb–O distance in the central $Sb_2(\mu\text{-}O)_2$ cycle, and a little longer than the Sb–O bonds in $Sb(OC_6H_3Me_2\text{-}2,6)_3$ (1.967–1.976 Å).[8] As a consequence of the formation of two donor–acceptor bonds, the conformation of the calix[4]arene changes from cone conformation to a flattened partial cone, similar to other main group metallocalixarenes.[11–13]

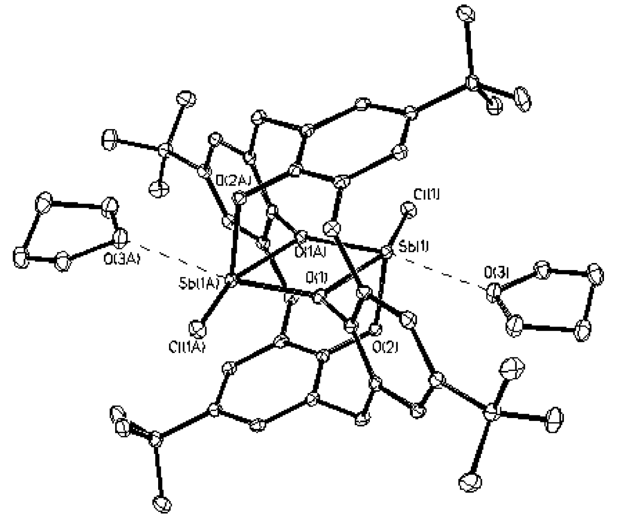
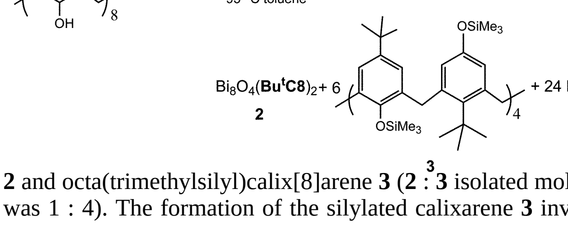


Fig. 1 An ORTEP view of **1**·4(THF) (30% probability). The H atoms and solvent THF molecules not involved in coordination of the Sb atom are omitted for clarity. Selected bond distances (Å) and angles (°): Sb(1)–O(2) 1.9882(16), Sb(1)–O(1A) 2.0274(16), Sb(1)–O(1) 2.4574(17), Sb(1)···O(3) 2.631(2), Sb(1)–Cl(1) 2.4220(6), O(2)–Sb(1)–O(1A) 88.82(7), O(2)–Sb(1)–Cl(1) 93.66(5), O(1A)–Sb(1)–Cl(1) 90.70(5), O(2)–Sb(1)–O(1) 80.72(6), O(1A)-Sb(1)–O(1) 65.79(7), Cl(1)–Sb(1)–O(1) 155.79(4), Sb(1A)–O(1)–Sb(1) 114.21(7), O(3)···Sb(1)–Cl(1) 84.00(7), O(3)···Sb(1)–O(1) 117.1(1), O(3)···Sb(1)–O(2) 77.0(1), O(3)···Sb(1)–O(1A) 164.5(1).

The analogous reaction of the **Bu^{t}C4** monoanion with $BiCl_3$ yielded intractable products, but the calix[8]arene complex of bismuth was readily obtained. Bi_8O_4(**Bu^{t}C8**)$_2$ **2** is a 2 nm polymetallic bismuth oxo aryloxide, synthesized by the reaction of **Bu^{t}C8** with bismuth amide ($Bi[N(SiMe_3)_2]_3$) in toluene at 95 °C [eqn. (1)]. This reaction gives a mixture of bismuth oxo calixarene



3

(1)

2 and octa(trimethylsilyl)calix[8]arene **3** (**2** : **3** isolated molar ratio was 1 : 4). The formation of the silylated calixarene **3** involves a trimethylsilyl shift from N to O, although the exact pathway to form **3** is not yet understood.[14,15] Compound **2** has good solubility in organic solvents and is quite air stable.[16] The ^1H NMR spectrum of **2** shows 3 pairs of doublets for methylene groups (5.60, 5.26, 4.22,

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† Electronic supplementary information (ESI) available: experimental details and ORTEP diagram of **2**. See http://www.rsc.org/suppdata/cc/b4/b404051a/

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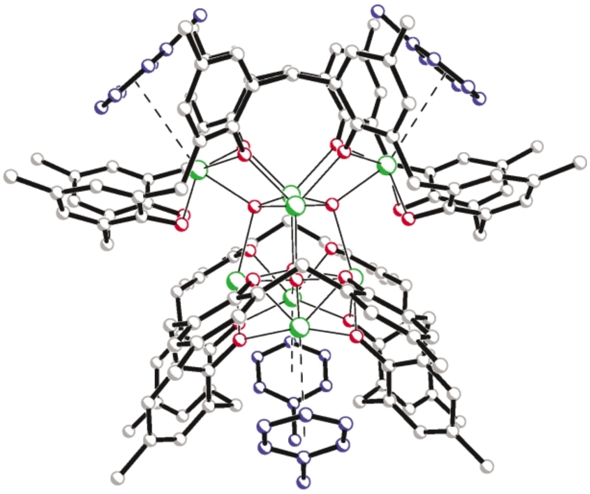
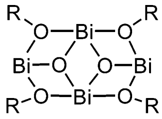


Fig. 2 The crystal structure of **2**·4(C_7H_8)·4(OC_4H_{10})·6(CH_3CN) (30% probability). The structure resides on a crystallographic $\bar{4}$ site. The H atoms and solvent OC_4H_{10} and CH_3CN molecules are omitted for clarity.

3.79, 3.36, and 2.73 ppm), 4 doublets for aromatic protons (7.56, 7.42, 7.36, and 7.33 ppm), and two singlets for *tert*-butyl groups (1.34 and 1.30 ppm) due to its high molecular symmetry.

Single crystals of **2**·4(C_7H_8)·4(OC_4H_{10})·6(CH_3CN) were obtained by fractional recrystallization from its toluene–THF–CH_3CN solution. The structure of **2**‡(Fig. 2 and 3) has $\bar{4}$ symmetry and consists of two **Bu^{t}C8** bismuth units linked to each other through bridging μ_4-O atoms (O(1), O(1A), O(1B), and O(1C)), probably formed from residual H_2O in the **Bu^{t}C8**.[17] The Bi_8O_{20} core of **2** exemplifies a structural trend noted by Whitmire and coworkers; **A** is a common $Bi_4O_2(OR)_4$ unit found in bismuth oxo alkoxide clusters.[18] If **2** is viewed as a 90°-rotated dimer of [Bi_4O_2**Bu^{t}C8**–8H] monomers, the core connectivity **A** can be discerned in each monomer unit.



A

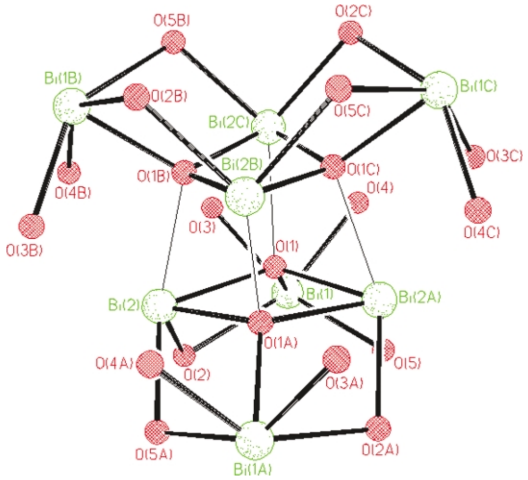


Fig. 3 The core structure of **2**·4(C_7H_8)4(OC_4H_{10})6(CH_3CN) (30% probability). Selected bond distance (Å) and angles (°): Bi(1)–O(1) 2.148(3), Bi(1)–O(4) 2.174(4), Bi(1)–O(3) 2.175(4), Bi(1)–O(5) 2.423(4), Bi(1)–O(2) 2.421(4), Bi(2)–O(5A) 2.235(4), Bi(2)–O(2) 2.244(4), Bi(2)–O(1A) 2.260(4), Bi(2)–O(1) 2.262(4), Bi(2)–O(1B) 2.482(4), O(1)–Bi(2)–O(1A) 66.44(15), O(1)–Bi(2)–O(2) 70.21(13), O(1)–Bi(2)–O(5A) 114.45(13), O(1)–Bi(2)–O(1B) 73.06(14).

Metal–metal distances within the bismuth oxygen core (Bi(1)···Bi(2) 3.6985(3) Å, Bi(2)···Bi(2A) 3.7670(3) Å and Bi(1)···Bi(2A) 3.6992(3) Å) are similar to those in the dimeric units of $Bi(OCH_2CH_2OMe)_3$.[19] The conformation of **Bu^{t}C8** is best described as a pinched cone, and the geometry at each five-coordinate bismuth(III) can be described as distorted square-based pyramidal. The Bi–O bond lengths (2.148(3)–2.482(4) Å) are normal.[19,20] The solvent toluene molecules fill empty spaces in the coordinated **Bu^{t}C8** ligands forming η^6 interactions with the Bi(1) atom (Fig. 2). The Bi–C distances (3.630(5)–3.942(5) Å) indicate a weak interaction.[19,20]

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Notes and references

‡ Crystal data for **1**·4(THF). $C_{68}H_{100}Cl_2O_{10}Sb_2$ M = 1391.88, triclinic, space group $P\bar{1}$, a = 10.7320(10) Å, b = 11.6398(11) Å, c = 13.9850(13) Å, α = 87.294(2)°, β = 72.496(1)°, γ = 83.252(1)°, V = 1654.4(3) Å^3, Z = 1, D_c = 1.397 Mg m^{-3}, T = 100(2) K, μ(MoKα) = 0.953 mm^{-1}, $wR2$ = 0.0908 (7286 independent reflections [R(int) = 0.0201]), $R1$ = 0.0341 [$I > 2\sigma(I)$]. Crystal data for **2**·4(C_7H_8)·4(OC_4H_{10})·6(CH_3CN). $C_{232}H_{298}Bi_8N_6O_{24}$ M = 5226.60, tetragonal, space group $I\bar{4}$, a = 18.2157(6) Å, b = 18.2157(6) Å, c = 32.180(2) Å, V = 10677.5(9) Å^3, Z = 2, D_c = 1.710 Mg m^{-3}, T = 100(2) K, μ(MoKα) = 6.638 mm^{-1}, $wR2$ = 0.0633 (12130 independent reflections [R(int) = 0.0414], $R1$ = 0.0294 [$I > 2\sigma(I)$]. The Flack parameter is 0.435(5) and **2** was treated as a racemic twin structure. CCDC 236034 and 238908. See http://www.rsc.org/suppdata/cc/b4/b404051a/ for crystallographic data in .cif format.

1 C. Floriani and R. Floriani-Moro, *Adv. Organomet. Chem.*, 2001, 167.
2 *Calixarenes 2001*, eds. Z. Asfari, V. Bohmer, J. Harrowfield and J. Vicens, Kluwer Academic Publishers, Boston, 2001.
3 B. G. McBurnett and A. H. Cowley, *Chem. Commun.*, 1999, 17.
4 T. Hascall, A. L. Rheingold, I. Guzei and G. Parkin, *Chem. Commun.*, 1998, 101.
5 D. C. Bradley, R. C. Methrotra, I. P. Rothwell and A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Academic Press, London, 2001.
6 T. A. Hanna, L. Liu, A. M. Angeles-Boza, X. Kou, C. D. Gutsche, K. Ejsmont, W. H. Watson, L. N. Zakharov, C. D. Incarvito and A. L. Rheingold, *J. Am. Chem. Soc.*, 2003, **125**, 6228.
7 A. J. Petrella, D. C. Craig, R. N. Lamb, C. L. Raston and N. K. Roberts, *Dalton Trans.*, 2004, 327.
8 G. A. Horley, M. F. Mahon, K. C. Molloy, M. M. Venter, P. W. Haycock and C. P. Myers, *Inorg. Chem.*, 2002, **41**, 1652.
9 G. G. Briand and N. Burford, *Chem. Rev.*, 1999, **99**, 2601.
10 T. A. Hanna, L. Liu, L. N. Zakharov, A. L. Rheingold, W. H. Watson and C. D. Gutsche, *Tetrahedron*, 2002, **58**, 9751.
11 V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *Polyhedron*, 1997, **16**, 4385.
12 M. G. Gardiner, S. M. Lawrence, C. L. Raston, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 2491.
13 J. L. Atwood, M. G. Gardiner, C. Jones, C. L. Raston, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 2487.
14 M. M. Olmstead, G. Sigel, H. Hope, X. Xu and P. P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 8087.
15 Treatment of *p-tert*-butylcalix[8]arene with $HN(SiMe_3)_2$ under our reaction conditions led to recovery of unreacted *p-tert*-butylcalix-[8]arene.
16 No decomposition was observed after the crystals sat for one month in ambient air at room temperature.
17 Several mechanisms have been proposed for bismuth oxo formation in cluster systems, however in this case residual water is the most plausible source of the oxo groups.
18 K. H. Whitmire, S. Hoppe, O. Sydora, J. L. Jolas and C. M. Jones, *Inorg. Chem.*, 2000, **39**, 85.
19 M.-C. Massiani, R. Papiernik, L. G. Hubert-Pfalzgraf and J.-C. Daran, *J. Chem. Soc., Chem. Commun.*, 1990, 301.
20 T. A. Hanna, G. Keitany, C. Ibarra, R. D. Sommer and A. L. Rheingold, *Polyhedron*, 2001, **20**, 2451.