Preliminary communication

The synthesis and structure of a new type of borosilicate cage

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Abstract

The novel borosilicate compound [^{t}BuSi{O(BC$_6$H$_4$Br)O}$_3$Si^{t}Bu], 1, which contains a Si(OBO)$_3$Si cage, is synthesised by the reaction of *tert*-butylsilanetriol with 4-bromophenylboric acid in toluene solution at reflux and structurally characterised with X-ray diffraction and spectroscopic techniques.

Keywords: X-ray diffraction; Cage; Boron; Borosilicate; Synthesis; Silicon

1. Introduction

All molecular borosilicates which have previously been structurally characterised by single-crystal X-ray methods have contained silicon atoms bonded in Si(-O-B)$_n$ units with $n = 1$ or 2. Examples of compounds with Si-O-B units include (Ph$_3$SiO)$_3$B [1], Ph$_3$SiOBOC(Me)$_2$CH$_2$CH(Me)O [2], and the cyclic compound PhB[(OSiPh$_2$)$_2$O]. [3,4] (all tricoordinate boron) and H$_2$N(CH$_2$)$_3$OB(Ph)(OSiR$_3$) (R$_3$ = Ph$_2$Me [5], PhMe$_2$) [6] (tetracoordinate boron). There were also two borosilicate cage compounds with three Si–O–B linkages at each boron atom, i.e. [B(OSiPh$_2$-OSiPh$_2$O)$_3$B] 2 [7] and the silasesquioxane-based species [((cyclo-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$B)$_2$] 3 [8], Schemes 1

and 2 respectively. The first of these cages was formed from the reaction between boric acid and (HO)SiPh$_2$OSiPh$_2$(OH); the second was formed from the reaction between boron triiodide and [(cyclo-C$_6$H$_{11}$)$_7$Si$_7$O$_9$(OH)$_3$], which contained three Si-OH groups. Compounds with Si(-O-B)$_2$-units include cyclic compounds such as [PhB(OSiR$_2$)O]$_2$ (R = Ph [4] or R = ^{t}Bu [9]). The novel type of borosilicate cage compound which we now report, [^{t}BuSi{O(BC$_6$H$_4$Br)O}$_3$-Si^{t}Bu], 1, Scheme 3, is the first example of a borosilicate compound containing an Si(-O-B)$_3$ unit to be studied crystallographically.
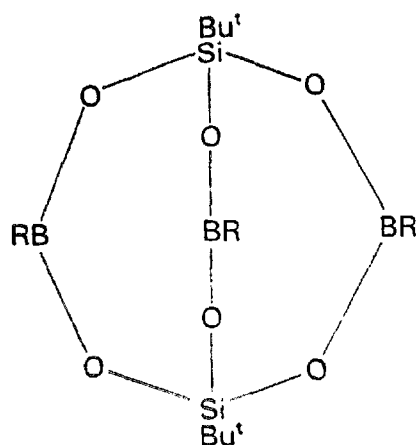
2. Results and discussion

To our knowledge, the reactions of silanetriols, RSi(OH)$_3$, with boron reagents have not previously been investigated, although the reaction of ^{t}Bu$_2$Si(OH)$_2$

Scheme 1. [B(OSiPh$_2$OSiPh$_2$O)$_3$B].
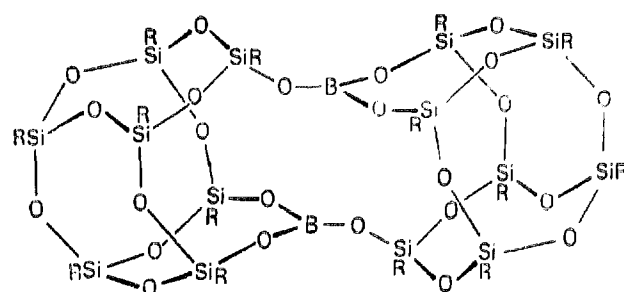
Scheme 2. [((cyclo-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$B)$_2$].

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Scheme 3. Compound 1 (R = *p*-C₆H₄Br).

with PhBCl₂ has been reported [9]. When ᵗBuSi(OH)₃ and 4-bromophenylboric acid are reacted in refluxing toluene solution in a 2:3 molar ratio for 20 h in a Dean–Stark apparatus, [ᵗBuSi{O(BC₆H₄Br)O}₃SiᵗBu], 1, is formed in 91% yield. Molecules of 1 contain two tetrahedral ᵗBuSiO₃-units and three trigonal planar BrC₆H₄BO₂-units held together by an 11-atom Si(OBO)₃Si cage, Fig. 1 and Table 1.

Crystal data and structure solution of 1. C₂₆H₃₀B₃Br₃O₆Si₂, $M = 766.84$, monoclinic, $P2_1/c$, $a = 16.738(2)$, $b = 9.782(2)$, $c = 21.130(3)$ Å, $\beta = 96.276(12)°$, $U = 3439.1(9)$ Å³, $Z = 4$, $D_c = 1.481$ g cm⁻³, λ(Mo Kα) = 0.7107 Å, μ(Mo Kα) = 3.623 mm⁻¹, $F(000) = 1528$, $T = 294$ K. Three-dimensional data were collected to a maximum θ of 25° with Mo radiation and a CAD4 diffractometer. The structure was solved by direct methods and refined by full-matrix

least squares calculations using all 6091 measured F^2 data and SHELXL93 [10]. All non-H atoms were allowed anisotropic motion and the H atoms were treated as riding atoms using SHELXL default distances (C–H = 0.93–0.96 Å). $R = 0.072$ for 2258 observed reflections $[I > 2\sigma(I)]$ and $wR(F^2)$ is 0.127 for all 6091 unique measured reflections. The max. and min. residual electron densities were 0.396 and -0.417 e Å⁻³. Full details have been deposited with the Cambridge Crystallographic Data Centre and are also available in CIF format from one author (GF).

The molecule has approximate D_{3h} symmetry with the silicon atoms located on the C_3 axis and the boron atoms in the σ_h plane. The B–O bond lengths in 1 are in the range 1.345(9) to 1.372(10) Å with a mean value of 1.362 Å, Table 1. The Si–O distances are between 1.614(5) and 1.628(5) Å, mean 1.621 Å. These distances are within the reported ranges of similar bonds, i.e. 1.313(2) Å [11] to 1.374(7) Å [4] and 1.615(3) Å [4] to 1.655(5) Å [4] for B–O and Si–O respectively. The Si–C distances in 1 are 1.827(7) and 1.826(8) Å, which are significantly shorter (at the 3 × esd level) than 1.872(4) and 1.869(4) Å in the cyclic [PhB(OSiᵗBu₂)O]₂ species, 4 [9].

In 1, the O–B–O angles range from 119.9(8) to 124.0(8)° and may be compared with an O–B–O angle of 122.8(3)° in [PhB(OSiᵗBu₃)O]₂ [9]. The O–Si–O angles in 1 vary from 108.5(3) to 109.7(3)°, Table 1. In 4, this was 111.5(1)° [9]. The B–O–Si angles in 1 vary from 137.5(6) to 140.7(6)°, and fall approximately midway in the reported range of such angles, i.e. 128.89(14) [3] to 160.9(3)° [4]. Two B–O–Si angles were reported in 4, 149.1(3) and 149.9(2)°, and both were significantly larger than those in 1. The data for 1 are very similar to
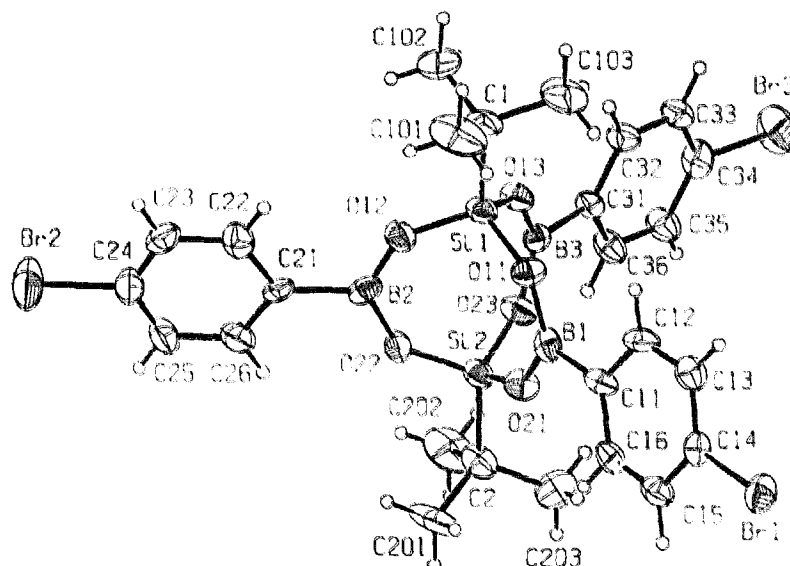

Fig. 1. An ORTEP plot (with 30% ellipsoids for non-H atoms) showing a general view of 1 and our atom numbering scheme.

Table 1
Selected interatomic dimensions in 1 (distances (Å), angles (deg))

Si(1)-O(11)	1.621(5)	Si(1)-O(12)	1.620(5)	Si(1)-O(13)	1.623(5)
Si(2)-O(21)	1.614(5)	Si(2)-O(22)	1.628(5)	Si(2)-O(23)	1.621(5)
Si(1)-C(1)	1.827(7)	Si(2)-C(2)	1.826(8)		
B(1)-O(11)	1.372(10)	B(1)-O(21)	1.365(10)	B(2)-O(12)	1.364(11)
B(2)-O(22)	1.355(10)	B(3)-O(13)	1.345(9)	B(3)-O(23)	1.372(9)
B(1)-C(11)	1.541(11)	B(2)-C(21)	1.573(11)	B(3)-C(31)	1.585(11)
C(14)-Br(1)	1.890(8)	C(24)-Br(2)	1.899(9)	C(34)-Br(3)	1.890(7)
O(11)-Si(1)-O(12)	109.7(3)	O(11)-Si(1)-O(13)	109.0(3)	O(12)-Si(1)-O(13)	108.8(3)
O(21)-Si(2)-O(22)	108.9(3)	O(21)-Si(2)-O(23)	108.8(3)	O(22)-Si(2)-O(23)	108.5(3)
O(11)-Si(1)-C(1)	109.8(4)	O(12)-Si(1)-C(1)	110.0(3)	O(13)-Si(1)-C(1)	109.4(3)
O(21)-Si(2)-C(2)	108.6(4)	O(22)-Si(2)-C(2)	111.1(3)	O(23)-Si(2)-C(2)	110.9(3)
O(11)-B(1)-O(21)	119.9(8)	O(12)-B(2)-O(22)	124.0(8)	O(13)-B(3)-O(23)	122.8(8)
O(11)-B(1)-C(11)	120.7(8)	O(21)-B(1)-C(11)	119.4(9)	O(12)-B(2)-C(21)	119.4(8)
O(22)-B(2)-C(21)	116.6(9)	O(13)-B(3)-C(31)	120.0(7)	O(23)-B(3)-C(31)	117.1(8)
B(1)-O(11)-Si(1)	139.6(6)	B(1)-O(21)-Si(2)	140.7(6)	B(2)-O(12)-Si(1)	137.5(6)
B(2)-O(22)-Si(2)	137.5(6)	B(3)-O(13)-Si(1)	137.7(5)	B(3)-O(23)-Si(2)	138.7(5)

those in the 17-atom B(OSiOSiO)$_3$B cage borosilicate, [B(OSiPh$_2$OSiPh$_2$O)$_3$B], **2** Scheme 1, which were between 137.89(18) and 140.03(18)° [7].

When viewed along the axis passing through the two silicon atoms, the *tert*-butyl groups are in an almost eclipsed arrangement, Fig. 2. The bromophenyl groups adopt a paddle wheel arrangement perpendicular to the Si $\cdots$ Si axis. The interplanar angles between the planes containing the O(1n)O(2n)B(n)C(1n) sequence and those containing the corresponding B(n)C(1n–6n) sequence are $-13.8(0.4)°$, $-8.4(0.4)°$, and $+11.3(0.4)°$

for the O$_2$BC$_6$ groups based on $n = 1$, 2, and 3 respectively. The intramolecular distances are, Si(1) $\cdots$ Si(2), 3.492(3) Å, B(1) $\cdots$ B(2), 3.832(14) Å, B(1) $\cdots$ B(3), 3.722(13) Å and B(2) $\cdots$ B(3), 3.766(13) Å. In the crystal, adjacent molecules of 1 make only van der Waals' contacts.

We have synthesised the 'parent' cage compound, ['BuSi{O(BPh)O}$_3$Si'Bu], but have not yet obtained crystals suitable for X-ray analysis. We are currently synthesising analogous cages with other groups attached at boron and silicon.
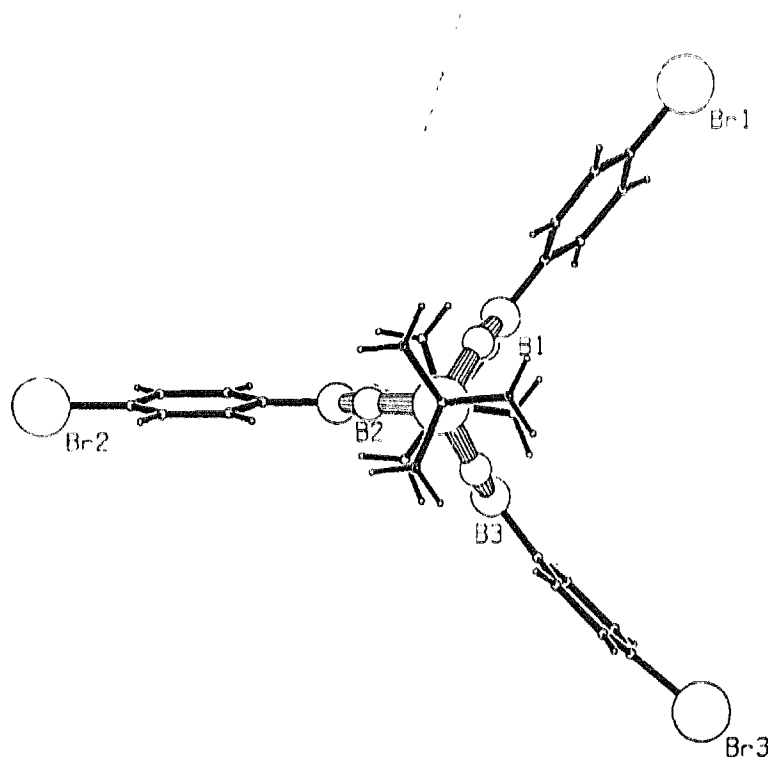

Fig. 2. A PLUTON plot of 1 viewed from above the Si(1)–Si(2) axis.

3. Experimental

3.1. Synthesis of ['BuSi{O(BC₆H₄Br)O}₃Si'Bu], 1

The silanetriol, $^{t}BuSi(OH)_{3}$, was synthesised from the corresponding trichloride by a literature method [12]. A mixture of *tert*-butylsilanetriol (0.400 g, 2.94 mmol) and 4-bromophenylboric acid (0.884 g, 4.40 mmol) in toluene (40 ml) was heated at the reflux temperature of the solution in a Dean–Stark apparatus for 20 h. After cooling the solution and removal of toluene (rotary evaporator, 35 °C), the white solid was dissolved in hexane. Crystallisation from hexane solution afforded ['BuSi{O(BC₆H₄Br)O}₃Si'Bu], 1 (1.019 g, 90.6%) m.p. 200–202 °C. (Found: C, 40.90; H, 4.00; Br, 31.00. $C_{26}H_{30}B_{3}Br_{3}O_{6}Si_{2}$ requires C, 40.70; H, 3.90; Br, 31.25%). IR (KBr disc, ν_{max} cm⁻¹) 2957 m, 1587 m, 1398 s, 1301 vs, 1130 vs, 1012 s, 891 m, 849 m, 825 m, 726 m, 705 s, 648 m, 615 s. ²⁹Si CPMAS NMR (Chemagnetics CMX 300 MHz Spectrometer, spin speed of 4 kHz, referenced to Si[SiMe₃]₄) $\delta = -95.0$ ppm.

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