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Synthesis and characterization of a novel eight-membered cyclo-1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane and 4,4'-bipyridine, 1D adduct

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ABSTRACT

Simple adducts of cyclo-diboradisiloxanes (Lewis acid) and amines (Lewis base) have been reported in the literature. However, the method for the synthesis of an 8-membered cyclo-diboratetrasiloxane, as well as its adducts, was modified in this report to save cost and achieve new results. In the literature, the synthesis of cyclo-1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane ($Ph_6B_2Si_2O_4$) (3) has been reported using diphenylsilanediol and phenylboronic acid and a Dean-Stark apparatus for the removal of water. However, in this study, molecular sieves were used for the facile removal of water, and the crude product recrystallized from diethyl ether and petroleum ether (3:1 ratio) to give compound 3. Compound 3 was reacted with 4,4'-bipyridine in a mixture of diethyl ether and petroleum ether solvents at reflux to give a 1D polymer $[Ph_6B_2Si_2O_4]\cdot L_1$ (4). Furthermore, compound 4 was characterized with various characterization methods such as single-crystal XRD, nuclear magnetic resonance, and FT-IR spectroscopy. The single crystal X-ray diffraction studies shows that the title compound crystalizes in the triclinic crystal system in the centrosymmetric space group P-1, a = 10.9372(4) Å, b = 18.4221(6) Å, c = 19.4697(6) Å, α = 70.533(3)°, β = 86.476(3)°, γ = 88.517(3)°, V = 3691.6(2) Å^3, Z = 2, T = 173.0 K, μ(MoKα) = 0.122 mm^{-1}, $Dcalc$ = 1.204 g/cm^3, 21463 reflections measured (5.196° ≤ 2Θ ≤ 56.45°), 14525 unique (R_{int} = 0.0185, R_{sigma} = 0.0483) which were used in all calculations, the final R_1 was 0.0721 (I > 2σ(I)) and wR_2 was 0.2143 (all data) with the 8-membered cyclo-1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane ($Ph_6B_2Si_2O_4$) (3) configuration.

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1. Introduction

Inorganic cyclic systems such as borasiloxanes (B-O-Si), in addition to being highly attractive in appearance, also serve as important systems with a wide range of applications arising from their fascinating magnetic and optical properties, electronic structures, potential quasi-aromatic character, and the ability to form extended π-π intra- and intermolecular interactions [1]. In principle, rings of the general formula $B_nSi_mO_{n+m}$, will have 2(n + m) π-electrons available for delocalization from the oxygen lone pairs. If n + m = 3, the Hückel criterion of 6 π-electrons is met, while if n + m = 4, an anti-aromatic 8 π-electron count results [2]. Furthermore, the ring systems (B-O-Si) and (Si-O-Si) have been used as molecular building blocks in the construction of metal-organic frameworks (MOFs) [3-9], covalent organic frameworks (COFs) [3,10,11] and other supramolecular compounds such as silsesquioxanes [10]. Compounds containing Si-O-B and O-B-O abound in the literature [12], and the Si-O, B-O, and C-O bond energies are 452, 536 and 358 kJ/mol, respectively. Thus, the Si-O and B-O bonds are stronger than the typical C-O bond energy. A good number of these compounds possess and display unusual high elasticity when a stress is suddenly applied, as well as high plasticity when the stress is applied slowly [13]. These compounds containing Si-O-B and O-B-O exist in the form of metaboronic acid, six-, eight-, or ten-member cages, cyclo-borosiloxane derivatives, or borosilicate cages, as well as large rings as shown in Figure 1 [12,14].

Borosilicate scaffolds have promising applications as building blocks in supramolecular chemistry. For example, Hunt *et al.* [15] and Pascu *et al.* [16] reported the use of an 8-membered borosilicate cage whose nodes were used for the synthesis of a 3-D system (COF-202) and macrocycles, respectively. Liu *et al.* [17] used the same principle for the synthesis of π-extended polymeric borosilicate cages used as sensors for volatile organic amines. Gopalakrishnan *et al.* [18] reported the synthesis, structure, photophysical, and other calculations for a series of eight-membered cyclic-borasiloxanes wherein the crystal packing pattern displayed noncovalent interactions. Recently, the synthesis of cage-like cyclic borosilicates based on boronic acid and the potential application in the assembly of triphenylboroxine and piperazine was reported [19,20].

Despite the myriad of applications for borosilicates and borosilicate adducts, only a few synthetic strategies for cyclic and cage-like molecular borosilicates and adducts are known. The reason for this may be mainly due to (i) the few commercially available silanols, (ii) the structural modifications of these compounds are difficult, and (iii) problems associated with stability [19].

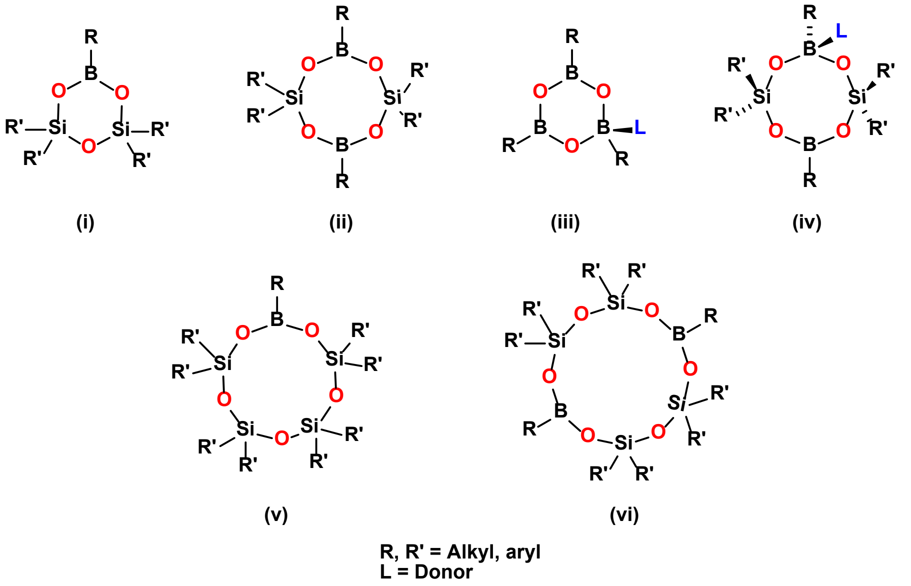
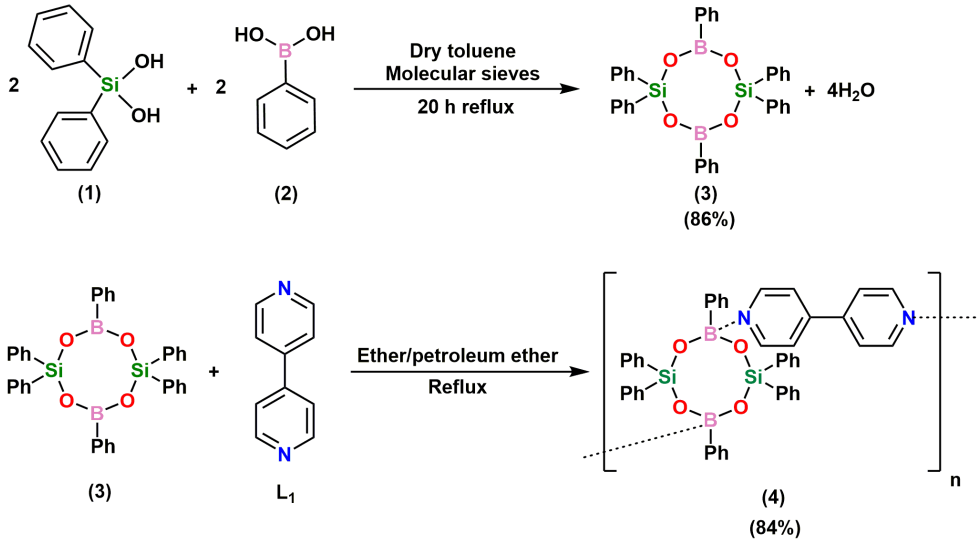


Figure 1. Structures of (i) 6-membered cyclo-boradisiloxane; (ii) 8-membered cyclo-diboradisiloxane; (iii) 1:1 adduct of a boroxine; (iv) 1:1 adduct of a cyclo-diboradisiloxane; (v) 10-membered cyclo-diboratetrasiloxane; (vi) 12-membered cyclo-diborahexasiloxane.



Scheme 1. Preparation of ($Ph_6B_2Si_2O_4$) (**3**) and [$Ph_6B_2Si_2O_4$]·L_1 (**4**) adduct.

The basic methods used in the synthesis of these borasiloxanes rings involve the cyclocondensation reaction of appropriate organoboronic acids and Si-containing precursors such as dihydroxysiloxanes, diethoxysilanes, and α,ω-dihydrosiloxanes as well as the condensation of dichlorophenylborane with dihydroxysilanes [12,21,22]. Solvents used include dry toluene, triethylamine, sodium-dried-benzene, or a mixture of solvents under a nitrogen atmosphere in which water is continuously removed using a Dean-Stark apparatus because these reactions are readily reversible. In this study, we report the synthesis and characterization of an eight-membered cyclodiboradisiloxane ring in which the boron atoms are tricoordinate (Lewis acid) and its further reaction with a 4,4'-bipyridine ligand (Lewis base) to give further coordination adducts possessing interesting properties [23].

In the literature, the synthesis of cyclo-1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane ($Ph_6B_2Si_2O_4$) (**3**) has been reported using diphenylsilanediol (**1**) and phenylboronic acid (**2**) and a Dean-Stark apparatus for the removal of water, with a reported 87% yield of compound **3** [2]. However, in the current research, molecular sieves were used for the removal of water and after the study, compound **3** was reacted with 4,4'-bipyridine to give a 1D polymer (**4**) adduct as shown in Scheme 1. Thus, the purpose of this research is to synthesis this eight-membered ring, characterize the eight-membered ring and then ligate it with a 4,4'-bipyridine ligand to give further coordination adducts with extended π-π stacking interactions.

2. Experimental

2.1. Chemicals and reagents

All chemicals, reagents, and solvents were purchased from Sigma-Aldrich or Alfa-Aesar and used as received unless otherwise stated. Molecular sieves (1.6 mm rods and 0.4 nm pores) were preheated to dryness in the oven at 120 °C for two weeks prior to use.

Table 1. Crystal data and structure refinement for [$Ph_6B_2Si_2O_4$]·L_1 (**4**).

Compound	**[$Ph_6B_2Si_2O_4$]·L_1 (4)**
Empirical formula	$C_{69}H_{57}B_3N_3O_6Si_3$, 0.6($C_{10}H_8N_2$), 1.4($C_4H_{10}O$)
Formula weight (g/mol)	1338.35
Temperature (K)	173.0
Crystal system	Triclinic
Space group	P-1
a, (Å)	10.9372(4)
b, (Å)	18.4221(6)
c, (Å)	19.4697(6)
α (°)	70.533(3)
β (°)	86.476(3)
γ (°)	88.517(3)
Volume (Å^3)	3691.6(2)
Z	2
ρ_{calc} (g/cm^3)	1.204
μ (mm^{-1})	0.122
F(000)	1410.0
Crystal size (mm^3)	0.58 × 0.33 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection (°)	5.196 to 56.45
Index ranges	$-14 \le h \le 14$, $-21 \le k \le 24$, $-24 \le l \le 21$
Reflections collected	21463
Independent reflections	14525 [R_{int} = 0.0185, R_{sigma} = 0.0483]
Data/restraints/parameters	14525/293/909
Goodness-of-fit on F^2	1.033
Final R indexes [I≥2σ (I)]	R_1 = 0.0721, wR_2 = 0.1929
Final R indexes [all data]	R_1 = 0.0963, wR_2 = 0.2143
Largest diff. peak/hole (e.Å^{-3})	1.12/-0.90

2.2. Instrumentation

^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were recorded on Bruker Avance III HD 400 MHz or 500 MHz spectrometers in $CDCl_3$ solvent unless otherwise stated. The chemical shifts (δ) for ^{1}H and ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{11}B{^{1}H} are quoted in ppm with reference to Me_4Si and BF_3OEt_2. The coupling constants are reported in Hz. Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FTIR Spectrometer operating in ATR mode.

2.3. Synthesis

2.3.1. Preparation of $Ph_6B_2Si_2O_4$ (3)

Diphenylsilanediol (**1**) 1.082 g (5.0 mmol) was mixed with 0.609 g (5.0 mmol) of phenylboronic acid (**2**) in dry toluene (50 mL) and 0.5 g of molecular sieves in a round bottom flask containing a magnetic stirrer bar. The mixture was refluxed under N_2 for 20 h. Thereafter, the round bottom flask and its contents were cooled to room temperature. The cooled reaction mixture was filtered and the filtrate collected. The molecular sieves were washed with dry toluene (3×25 mL). The filtrates were combined and concentrated under reduced pressure, and the solid residue was recrystallized from diethyl ether and petroleum ether (3:1 ratio) to give compound **3**, 1.30 g, 86% (Lit. 87% [2]); M.p.: 162-163 °C (Lit. 161-162 °C [2]).

Cyclo-1, 3, 3, 5, 7, 7-hexaphenyl-1, 5-dibora-3, 7-disiloxane: Color: White. Yield: 86%. M.p.: 162.0-163.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.31-7.54 (m, 18H, *m*,*p*-C_6H_5), 7.73-7.75 (m, 8H *o*-C_6H_5Si), 8.08-8.10 (m, 4H, *o*-C_6H_5B). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 127.93, 128.06, 130.60, 131.74, 133.40, 134.12, 135.65 (C_6H_5Si, C_6H_5B). ^{11}B NMR (160 MHz, $CDCl_3$, δ, ppm): 25.69. ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, δ, ppm): -45.00. MS (70 eV, EI, *m/z*): 604 (M$^+$), 527 (M-Ph)$^+$, 423 (M-Ph-PhBO)$^+$, 406 (M-Ph_2SiO)$^+$. FT-IR (ATR, ν, cm^{-1}): 3023 (C-H aromatic), 1349 (B-O), 1307 (Si-C str.), 1071 (Si-O str.).

2.3.2. Preparation of [$Ph_6B_2Si_2O_4$]·L_1 (4)

In a round bottom flask, [$Ph_6B_2Si_2O_4$] (**3**), (0.25 g, 0.415 mmol) was added to 4,4'-bipyridine (L_1) (0.065 g, 0.415 mmol) and a mixture of solvents (diethyl ether 21 mL and petroleum ether 7 mL). The mixture was heated at reflux while stirring for 4 h. The resultant solution was allowed to cool to room temperature followed by filtration. The filtrate was transferred to a vial, covered with perforated parafilm, and stored in the fumehood for slow evaporation of the solvent. Colourless crystals were obtained from the mixture of diethyl ether and petroleum ether solvents after 12 h to give compound 4, [$Ph_6B_2Si_2O_4$]·L_1. Color: White. Yield: 84%. M.p.: 184-186 °C. FT-IR (ATR, ν, cm^{-1}): 3067 (C-H aromatic), 1429 (B-O), 1324 (C-N), 1059 (Si-O str.). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.32-7.56 (m, 18H, *m, p*-C_6H_5), 7.62-7.64 (m, 4H, *m*-C_5H_4N), 7.73-7.78 (m, 8H, *o*-C_6H_5Si), 8.09-8.17 (m, 4H, *o*-C_6H_5B), 8.80-8.82 (m, 4H, *o*-C_5H_4N). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 149.96, 145.87, 135.36, 134.30, 134.10, 133.72, 131.32, 127.94, 127.94, 127.82, 121.59. ^{11}B NMR (160 MHz, $CDCl_3$, δ, ppm): 20.91. ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, δ, ppm): -45.16.

3. Results and discussion

The eight-membered borasiloxane compound **3** was characterized using standard analytical and spectroscopic methods. Compound **3** is a colorless crystalline solid and readily soluble in nonpolar organic solvents such as hexane and benzene. The ^{1}H NMR spectrum of compound **3** shows well-resolved resonances with aromatic proton signals found within the range of δ 7.32-8.17 ppm, comparable to values reported in the literature [12,14,18]. The ^{13}C{^{1}H} NMR spectrum of compound **3** shows signals for aromatic carbons in the range of δ 127.93-135.65 ppm, which are also in agreement with the values in the literature [12,14,18]. The ^{11}B{^{1}H} NMR of compound **3** shows a broad singlet at δ 25.69 ppm, which is indicative of a single boron chemical environment. In the same way, the ^{29}Si NMR of compound **3** showed a singlet at δ -45.00 ppm. Furthermore, the IR spectrum obtained from compound **3** showed strong absorption peaks in the regions: 3023 cm^{-1}, νC-H; 1349 cm^{-1}, νB-O; 1307 cm^{-1}, νSi-C; 1071 cm^{-1}, νSi-O [24]. Subsequently, compound **3** was treated with 4,4'-bipyridine (L_1). Compound **4** crystallized in the triclinic unit cell with a space group of *P*-1. Crystallographic data, bond distance, and angle values are shown in Tables 1-3, respectively.

Table 2. Selected bond lengths for [$Ph_6B_2Si_2O_4$]·L_1 (**4**) *.

Atom	Atom	Length, Å	Atom	Atom	Length, Å	Atom	Atom	Length, Å	Atom	Atom	Length, Å
B1	O2	1.436(4)	O4	B5	1.437(4)	Si7	C61'	1.907(7)	O22	Si23	1.621(2)
B1	O8	1.427(4)	B5	O6	1.433(4)	N9	C10	1.331(4)	Si23	O24	1.610(2)
B1	N9	1.695(4)	B5	N25	1.695(4)	N9	C14	1.319(4)	Si23	C73	1.872(3)
B1	C31	1.633(4)	B5	C49	1.610(4)	N18	C19	1.331(4)	Si23	C79	1.872(3)
B1	C31'	1.665(10)	O6	Si7	1.614(2)	N18	B21	1.708(4)	O24	B21^{1}	1.433(4)
O2	Si3	1.609(2)	Si7	O8	1.610(2)	C19	C20	1.384(4)	N25	C26	1.322(4)
Si3	O4	1.611(2)	Si7	C55	1.880(3)	B21	O22	1.438(4)	N25	C30	1.322(4)
Si3	C37	1.866(3)	Si7	C55'	1.917(10)	B21	O24^{1}	1.433(4)			
Si3	C43	1.874(3)	Si7	C61	1.885(3)	B21	C67	1.609(5)			

* Symmetry code: ^{1} -*x*, 1-*y*, 2-*z*.

Table 3. Selected bond angles for [$Ph_6B_2Si_2O_4$]·L_1 (**4**).

Atom	Atom	Atom	Angle, °	Atom	Atom	Atom	Angle, °	Atom	Atom	Atom	Angle, °
O2	B1	N9	103.0(2)	O6	Si7	C55	104.60(17)	O24^{1}	B21	C67	115.4(2)
O2	B1	C31	114.5(2)	O6	Si7	C55'	108.8(5)	C67	B21	N18	102.0(2)
O2	B1	C31'	111.0(5)	O6	Si7	C61	107.0(2)	B21	O22	Si23	134.0(2)
O8	B1	O2	116.8(2)	O6	Si7	C61'	115.8(3)	O22	Si23	C73	105.51(12)
O8	B1	N9	105.3(2)	O8	Si7	O6	113.88(11)	O22	Si23	C79	109.63(11)
O8	B1	C31	111.9(2)	O8	Si7	C55	113.71(19)	O24	Si23	O22	113.68(11)
O8	B1	C31'	111.8(5)	O8	Si7	C55'	106.1(5)	O24	Si23	C73	106.64(12)
C31	B1	N9	103.5(2)	O8	Si7	C61	104.47(15)	O24	Si23	C79	111.01(13)
C31'	B1	N9	108.1(5)	O8	Si7	C61'	103.5(3)	C79	Si23	C73	110.16(13)
B1	O2	Si3	138.80(18)	C55	Si7	C61	113.2(2)	B21^{1}	O24	Si23	143.30(19)
O2	Si3	O4	113.21(11)	C61'	Si7	C55'	108.1(6)	C26	N25	B5	122.8(2)
O2	Si3	C37	111.00(12)	B1	O8	Si7	147.0(2)	C30	N25	B5	119.4(2)
O2	Si3	C43	107.53(12)	C10	N9	B1	121.0(2)	C30	N25	C26	117.7(3)
O4	Si3	C37	105.19(12)	C14	N9	B1	121.4(2)	N25	C26	C27	122.0(3)
O4	Si3	C43	112.58(11)	C14	N9	C10	117.5(3)	N25	C30	C29	123.1(3)
C37	Si3	C43	107.22(12)	C17	N18	B21	118.6(2)	C32'	C31'	B1	121.2(8)
B5	O4	Si3	133.44(19)	C19	N18	C17	118.7(3)	C36'	C31'	B1	118.7(8)
O4	B5	N25	102.4(2)	C19	N18	B21	122.5(2)	C38	C37	Si3	121.2(2)
O4	B5	C49	113.2(3)	N18	C19	C20	122.0(3)	C42	C37	Si3	121.0(2)
O6	B5	O4	115.4(2)	C19	C20	C15	119.7(3)	C91	O90	C93	113.9(7)
O6	B5	N25	105.5(2)	O22	B21	N18	105.8(2)	O90	C91	C94	116.4(9)
O6	B5	C49	112.8(3)	O22	B21	C67	113.0(3)	O90	C93	C92	107.8(7)
C49	B5	N25	106.2(2)	O24^{1}	B21	N18	102.7(2)	C123	O120	C121	125.3(16)
B5	O6	Si7	137.52(19)	O24^{1}	B21	O22	115.8(2)	O120	C121	C122	113.0(11)

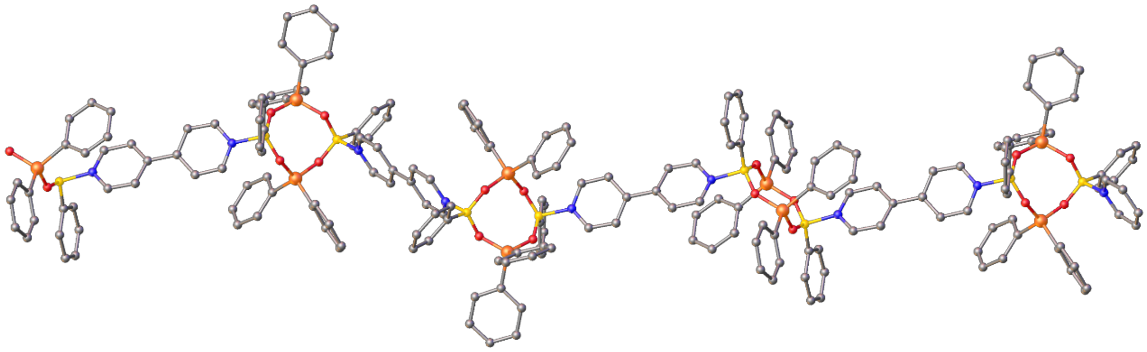


Figure 2. 1-D crystal structure of compound **4**. Yellow = B, brown = Si, grey = C, blue = N, red= O. H atoms are omitted for clarity.

Compound **4** is a 1-D borasiloxane/bipyridine polymer obtained as colourless crystals from the slow evaporation of diethyl ether and petroleum ether solvents mixture. At room temperature, compound **4** was soluble in organic solvents such as dichloromethane, ether, toluene and acetone. The $^{11}B\{^1H\}$ NMR spectrum of compound **4** showed a singlet at δ 20.91 ppm typical of 4-coordinate boron, while that of the starting material, compound **3** was δ 25.69 ppm typical of 3-coodinate B. Similarly, the $^{29}Si\{^1H\}$ NMR spectrum of compound **4** showed a singlet at δ -45.16 ppm and compound **3** was δ -45.00 ppm. Data obtained from a single crystal X-ray diffraction study show that compound **4** consists of an eight-membered ring structure derived from compound **3** with two B atoms coordinated to 4,4'-bipyridine (L_1), resulting in the formation of a 1-D polymer as shown in Figure 2.

The B-O-Si angles in compound **4** range from 133.44(19) to 147.0(2)° with an average value of 139.19(2)° and display some distortion at the O atoms as revealed in the ellipsoid plot Figure 3, and when compared with the B-O-Si angles of compound **3** (145.3(3) and 160.9(3)°) [2]. The four B-O distances in compound **4** are 1.426(4) Å (B1-O2), 1.427(4) Å (B1-O8), 1.437(4) Å (B5-O4), and 1.433(4) Å (B5-O6), and are longer than the B-O lengths for the tri-coordinated B in compound **3** ($Si_2B_2O_4$), which range from (1.36-1.39 Å) [13,18,24]. However, the values reported here are similar to other B-O distances for tetrahedrally coordinated B in compounds such as N(CH_2CH_2O)B (1.43(1) Å, [25]), $Ph_2BOCH_2CH_2NH_2$ (1.484(3) Å [26]) and Ph($OSiR_2R'$)B{OCH_2)$_3$N} (R or R' = Ph or CH_3) (1.439(4) Å and 1.461(3) Å [27]) and [Bu^{t}Si(OPhBO)$_3$SiBu^t]·NC_5H_5 (1.457(18) Å and 1.469(18) Å, [24]) where the B is directly bonded to two O atoms, a phenyl group, and the N atom. The observed longer bond length at the tetrahedrally bonded B site compared to the tri-coordinated B may be linked to a reduction in B-O π-bonding component on changing from trigonal to tetrahedral coordination geometry at the B.

Table 4. Intramolecular hydrogen bonds for compound **4** (Å, °).

Donor-H···Acceptor	**D-H**	**H···A**	**D···A**	**∠D-H···A**
C(10)-H(10A)···O(8)	0.95	2.50	2.8480(1)	102
C(14)-H(14A)···O(2)	0.95	2.42	2.7850(1)	103
C(19)-H(19A)···O(24)	0.95	2.37	2.7630(1)	104
C(26)-H(26A)···O(4)	0.95	2.34	2.7373(1)	105
C(42)-H(42A)···O(4)	0.95	2.58	3.0297(1)	109
C(54)-H(54A)···O(6)	0.95	2.55	2.9094(1)	103
C(66)-H(66A)···O(8)	0.95	2.57	3.0164(1)	109
C(72)-H(72A)···O(22)	0.95	2.58	2.9367(1)	103

Table 5. Geometrical parameters of C–H···π contacts for the compound **4** (Å, °) *.

C-H(I)···Cg(J)	**Symmetry**	**H···Cg**	**H-Perp**	**Gamma**	**X-H···Cg**	**X···Cg**
C(105)-H(10D)···Cg(15)	*x*, *y*, *z*	2.68	2.33	29.73	143	3.4840(1)
C(13)-H(13A)···Cg(6)	1-*x*, -*y*, 2-*z*	2.85	2.73	16.60	135	3.5928(1)
C(20)-H(20A)···Cg(5)	1-*x*, -*y*, 2-*z*	2.88	-2.87	4.60	130	3.5613(1)
C(66'-H(66B)···Cg(3)	*x*, *y*, *z*	2.83	2.78	10.50	119	3.3895(1)

* Cg(3): N(25)-C(26)-C(27)-C(28)-C(29)-C(30); Cg(5): C(37)-C(38)-C(39)-C(40)-C(41)-C(42); Cg(6): C(43)-C(44)-C(45)-C(46)-C(47)-C(48); Cg(15): C(61')-C(62')-C(63')-C(64')-C(65')-C(66'); Cg(J) = Center of gravity of ring J; H-Perp = Perpendicular distance of H to ring plane J; Gamma = Angle between Cg-H vector and ring J normal; X-H···Cg = X-H-Cg angle (degrees); X···Cg = Distance of X to Cg (Angstrom).

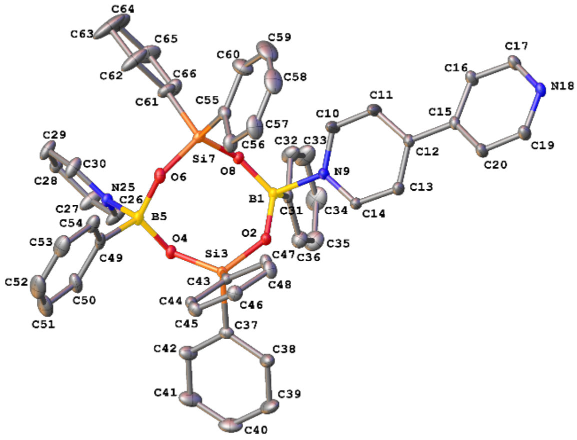


Figure 3. An ellipsoid view of a fragment of $[Ph_6B_2Si_2O_4]\cdot L_1$ (**4**) with some atom labelling. Yellow = B, brown = Si, grey = C, blue = N, red= O. H atoms are omitted for clarity.

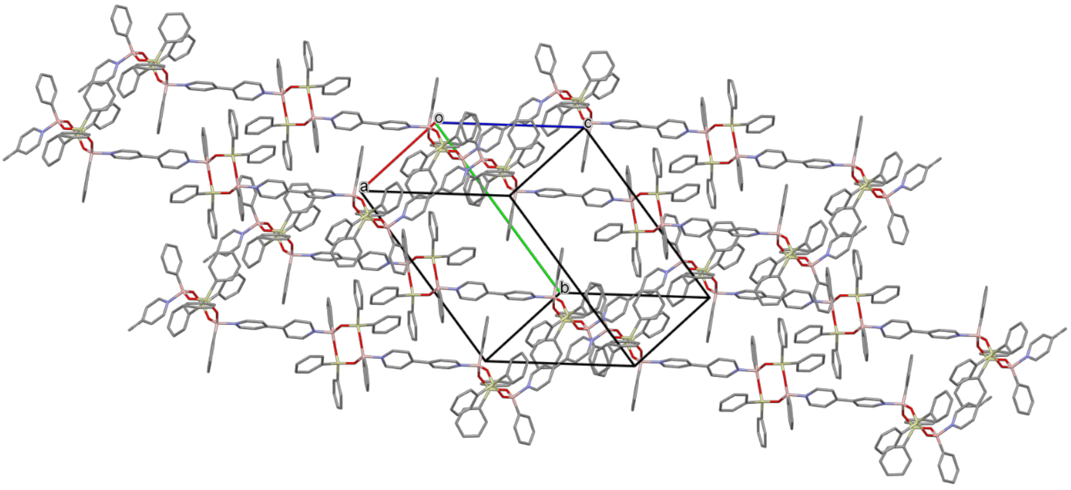


Figure 4. Crystal packing in $[Ph_6B_2Si_2O_4]\cdot L_1$(**4**) with four polymeric chains running parallel to the a-axis leading to formation of channels**.** Colour identity, pink = B, green = Si, grey = C, blue = N, red= O. H atoms and disordered solvent molecule are omitted for clarity.

In addition, the four Si-O bond lengths in compound **4** range from 1.606(2) to 1.614(2) Å, and are relatively short compared to the lengths of Si-O bonds in the literature for a tetra-coordinate Si bonded to two O atoms and two carbon atoms with a mean value of 1.645 Å [18,24]. However, some Si-O bond distances similar to those reported here have been observed in the literature (1.585 to 1.634 Å) [24,27]. The shorter Si-O distances associated with compound **4** suggest an increase in the electron density in the Si-O bond, which is also consistent with the decrease in the electron density of B-O.

The B-N bond lengths in compound **4** are 1.695(4) and 1.708(4) Å with an average value of 1.702(4) Å. For a simple borosiloxane such as $Ph(OSiR_2R')B\{OCH_2)_3N\}$ (R or R′ = Ph or CH_3) [27] and $[Bu^tSi(OPhBO)_3SiBu^t]\cdot NC_5H_5$ [24], the B-N distances reported were 1.639 Å and 1.655 Å, respectively. However, values of 1.556, 1.651, 1.653, 1.654, 1.676, 1.679, 1.681, and 1.688 Å have been reported elsewhere in the literature for B-N bond length in boroxine adducts for which the B atoms were also tetra-coordinated [28-34]. The Si-C bond lengths in compound **4** range from 1.866(3) to 1.885(3) Å with an average of bond distance of 1.877(3) Å. These are as expected for single Si-C bonds [18,24,27].

The internal ring angles O2-B1-O8 and O4-B5-O6 are 116.8(2)° and 115.4(2)°, respectively, with a mean value of 116.1(2)°. These angles in compound **4** at the B centres are higher than 109.5° expected for a tetrahedral geometry, but a similar observation has been reported in the literature [24]. Similarly, the O2-Si3-O4 and O6-Si7-O8 angles are 113.21(11)° and 113.88(11)°, respectively, with a mean value of 113.6(11)°, which is also slightly higher than 109.5° expected for a tetrahedral silicon. The bond angles at the Si centre as well as the Si-C bonds are comparable to other borasiloxane compounds and simple adducts in the literature [18,24,35].

In addition to the covalent and dative bonds found in compound **4**, the crystal packing (Figure 4) of the compound also shows intramolecular interactions. The parameters of the intramolecular short contacts for compound **4** are given in Table 4. Similar non-covalent interactions have been reported in cycloborasiloxane of eight-membered rings [18]. The various intermolecular and intramolecular interactions give rise to chains running parallel to the *a*-axis and crosslinking to form potential channels. Detailed geometric information of C-H···π stacking contacts of compound **4** is given in Table 5.

4. Conclusions

In this article, Lewis acid cyclo-1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane ($Ph_6B_2Si_2O_4$) (**3**), has been successfully synthesized and the structure confirmed by standard analytical and spectroscopic techniques. Following this synthesis, a 4,4'-bipyridine, which acted as a Lewis base, was complexed with compound **3** to give a 1D polymeric structure $[Ph_6B_2Si_2O_4]\cdot L_1$ (**4**). This novel 1D polymeric material has been characterized by standard analytical and spectroscopy methods. The polymer has channels in its packing and possesses inter molecular and intramolecular π-π interactions as well as other interactions such hydrogen bonding.

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Supporting information S

CCDC-2356307 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement DS

Conflict of interest: The authors declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have been adhered to.
Sample availability: Samples of the compounds are available from the author.

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Conceptualization: Okpara Sergeant Bull, Chioma Don-Lawson; Methodology: Okpara Sergeant Bull; Formal Analysis: Okpara Sergeant Bull; Investigation: Okpara Sergeant Bull; Resources: Chioma Don-Lawson; Data Curation: Okpara Sergeant Bull; Writing - Original Draft: Okpara Sergeant Bull; Writing -Review and Editing: Ugo Nweke-Maraizu; Visualization: Ugo Nweke-Maraizu; Funding acquisition: Chioma Don-Lawson; Supervision: Okpara Sergeant Bull; Project Administration: Ugo Nweke-Maraizu.

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