

Polymeric chains from  $[(\text{Ph}_2\text{SiOLi} \cdot \text{THF})_2\text{O}]_2$  and linear dicoordinating nitrogen bases. Crystal X-ray structures of  $[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot \text{THF}]_2 \cdot 2\text{DABCO}$ , DABCO = 1,4-diazabicyclo[2.2.2]octane, and  $[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot \text{THF}]_2 \cdot 2\{4,4'\text{-bipyridine}\}$

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Abstract

The new compounds  $[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot (\text{C}_4\text{H}_8\text{O})]_2(\text{C}_6\text{H}_{12}\text{N}_2)_x$  ( $\text{C}_6\text{H}_{12}\text{N}_2 = \text{DABCO} = 1,4\text{-diazabicyclo[2.2.2]octane}$ ) and  $[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot (\text{C}_4\text{H}_8\text{O})]_2 \cdot 2(\text{C}_{10}\text{H}_8\text{N}_2)_x$  ( $\text{C}_{10}\text{H}_8\text{N}_2 = 4,4'\text{-bipy} = 4,4'\text{-bipyridine}$ ) have been synthesised using the dilithium salt  $[(\text{Ph}_2\text{SiOLi})_2\text{O}]_2$  in the presence of the Lewis bases DABCO and 4,4'-bipy respectively. Their solid-state structures have been determined by single-crystal X-ray diffraction. Comparisons between these compounds and the related pyridine (py) adduct  $[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot 2\text{py}]_2$  and dioxane adduct  $[(\text{Ph}_2\text{SiOLi})_2\text{O}]_2 \cdot 3(\text{C}_4\text{H}_8\text{O}_2)_x$  are discussed.

Keywords: Silicon; Metallasiloxane; Lithium; Crystal structure

1. Introduction

Many compounds incorporating metallasiloxane rings have been reported in the literature recently [1]. We have for some time been investigating compounds incorporating the disiloxanediolate fragment  $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$  derived from the disiloxanediolate precursor  $[(\text{Ph}_2\text{SiOLi})_2\text{O}]_2$  [2]. In earlier papers we reported on the solid-state structures of this precursor in the presence of the Lewis bases pyridine and 1,4-dioxane, resulting in the molecular and polymeric adducts  $[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot 2\text{py}]_2$  (1) [3] and  $[(\text{Ph}_2\text{SiOLi})_2\text{O}]_2 \cdot 3(\text{C}_4\text{H}_8\text{O}_2)_x$  (2) [2f] respectively. We were interested to see whether variations on structure 2 [2f] could be brought about by changing the linear dicoordinating base. To this end we initially investigated the dinitrogen base DABCO which has similar linear distance (2.60 Å) between the donor nitrogen atoms to that between the

oxygen atoms (2.76 Å) in dioxane. We subsequently investigated the dinitrogen base 4,4'-bipyridine in which the distance (7.10 Å) between donor nitrogens is considerably longer. We now report on the solid-state structures of the DABCO and 4,4'-bipy adducts  $[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot (\text{C}_4\text{H}_8\text{O})]_2(\text{C}_6\text{H}_{12}\text{N}_2)_x$  (3) and  $[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot (\text{C}_4\text{H}_8\text{O})]_2 \cdot 2(\text{C}_{10}\text{H}_8\text{N}_2)_x$  (4) respectively.

2. Results and discussion

2.1. Synthesis

The synthetic route employed is essentially the same for all the adducts. Generally, it involves treating a solution of tetraphenyldisiloxanediol in toluene with *n*-butyllithium in hexane in a 1:2 molar ratio, followed by the addition of the Lewis base. Compounds 3 and 4 are moisture-sensitive colourless crystalline solids which are sparingly soluble in hydrocarbon and aromatic solvents.

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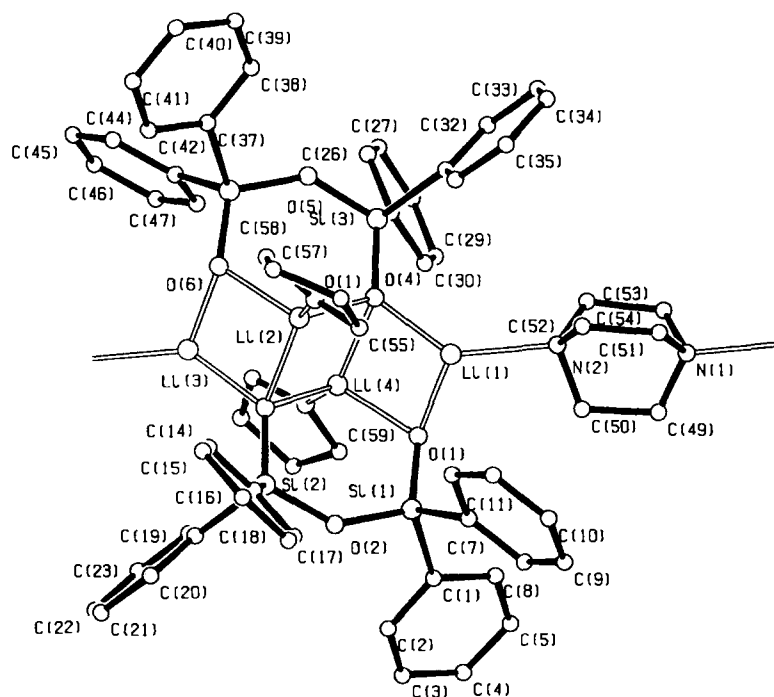


Fig. 1. Chain structure of  $[\{(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot (\text{C}_4\text{H}_8\text{O})\}_2(\text{C}_6\text{H}_{12}\text{N}_2)]_n$  (3) (phenyl, THF and DABCO hydrogen atoms omitted).

## 2.2. Crystal structures

The solid-state structure of the pyridine adduct of dilithium tetraphenyldisiloxanediolate  $[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot 2\text{py}]_2$  (1) is dimeric [3], consisting of a pentacyclic unit comprised of two six-membered lithiodisiloxane rings and a folded ladder arrangement of three four-membered lithio-oxane rings. This type of folded ladder arrangement is not unique to these adducts. In fact, it is also found in the complexed lithium amides

$[(\text{H}_2\text{C}(\text{CH}_2)_3\text{NLi})_3 \cdot \text{PMDETA}]_2$  and  $[(\text{H}_2\text{C}(\text{CH}_2)_3\text{NLi})_2 \cdot \text{TMEDA}]_2$  (PMDETA = N,N,N',N',N''-penta-methyldiethylenetriamine, a potential tridentate chelating ligand, and TMEDA = N,N,N',N'-tetramethylethylenediamine) [4], but in these cases the ladder consists of three four-membered  $(\text{Li}-\text{N})_2$  rings. The lithium phosphides  $[(\text{Me}_3\text{Si})_2\text{PLi}]_4 \cdot 2\text{THF}$  [5] and  $[(\text{tBu}_2\text{PLi})_4 \cdot 2\text{THF}]$  [6] have also been structurally characterised and found to contain a  $\text{P}_4\text{Li}_4$  laddering framework (although not a folded one).

Table 1

Comparison of molecular parameters of pyridine, 1,4-dioxane, DABCO and 4,4'-bipyridine adducts of dilithium tetraphenyldisiloxanediolate 1, 2, 3 and 4 respectively

	1	2	3	4
<i>Average bond lengths (Å)</i>				
Si–O(Si)	1.638	1.634	1.635	1.631
Si–O(Li)	1.583	1.591	1.584	1.578
$\text{Li}_{\text{exo}}-\text{Li}_{\text{endo}}$	2.472	2.405	2.455	2.450
$\text{Li}_{\text{endo}}-\text{Li}_{\text{endo}}$	2.506	2.531	2.515	2.549
$\text{Li}_{\text{exo}}-\text{O}$	1.837	1.848	1.862	1.958
$\text{Li}_{\text{endo}}-\text{O}$	1.982	1.946	2.008	1.971
<i>Average bond angles (°)</i>				
O–Si–O	112.34	111.65	112.32	111.70
Si–O–Si	138.86	140.20	140.05	141.90
Geometry at $\text{Li}_{\text{exo}}$	Distorted Trigonal	Distorted Trigonal	Distorted Trigonal	Distorted Tetrahedral
Geometry at $\text{Li}_{\text{endo}}$	Distorted Tetrahedral	Distorted Tetrahedral	Distorted Tetrahedral	Distorted Tetrahedral
Max. atomic deviation of mean $\text{LiO}_3\text{Si}_2$ plane	0.356 Å	0.436 Å	0.276 Å	0.302 Å

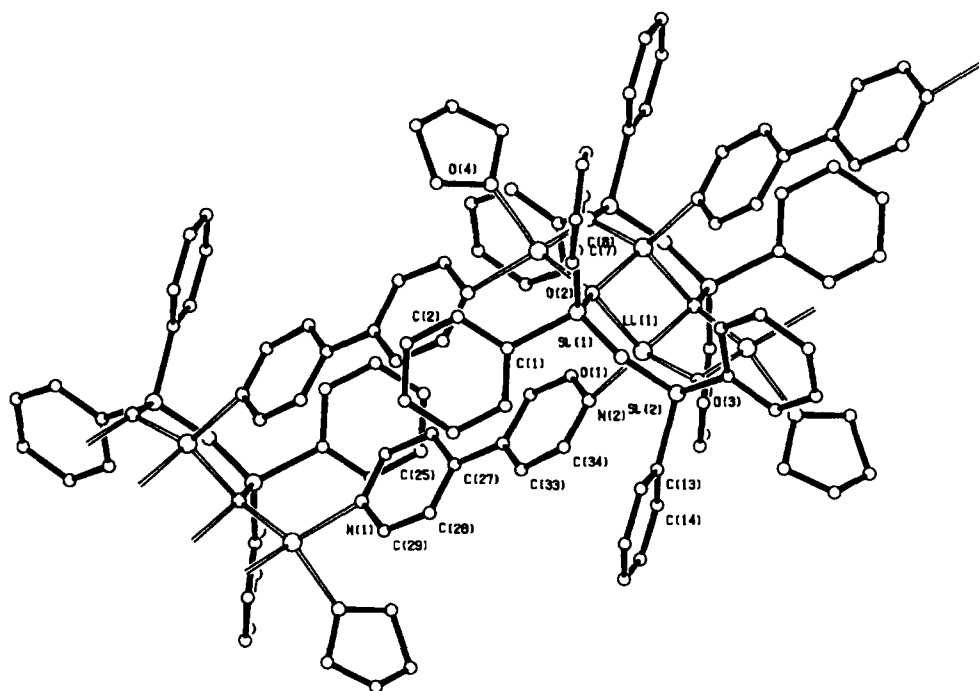


Fig. 2. Polycyclic linear chain structure of  $[\{(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot (\text{C}_4\text{H}_8\text{O})\}_2 \cdot 2(\text{C}_{10}\text{H}_8\text{N}_2)]_n$  (**4**) (phenyl rings, THF and 4,4'-bipyridyl hydrogen atoms omitted).

The basic skeletal framework found in **1** is also present in the dioxane adduct  $[\{(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot 3(\text{C}_4\text{H}_8\text{O}_2)\}_n$  (**2**). However, in this case the dimeric units are connected by a dioxane bridge, through the exocyclic bridging lithium atoms forming polymeric

chains. The two endocyclic lithium atoms each have a dioxane molecule coordinated in a terminal unidentate fashion [2f].

DABCO and 1,4-dioxane are similar in that both have ethylene ( $-\text{CH}_2\text{CH}_2-$ ) bridges between two dia-

Table 2  
Crystal data, intensity measurements and structure refinement for compounds **3** and **4**<sup>a</sup>

	<b>3</b>	<b>4</b>
Formula	$\text{C}_{62}\text{H}_{68}\text{Li}_4\text{N}_2\text{O}_8\text{Si}_4$	$\text{C}_{38}\text{H}_{36}\text{Li}_2\text{N}_2\text{O}_4\text{Si}_2$
Formula weight	1109.30	695.70
Crystal system	Monoclinic	Monoclinic
Space group	$P_{21}$	$P_{21/n}$
$a$ (Å)	11.924(2)	13.3080(10)
$b$ (Å)	21.258(2)	17.729(2)
$c$ (Å)	12.6570(10)	17.885(2)
$\beta$ (°)	103.820(10)	94.730(10)
Volume (Å <sup>3</sup> )	3115.4(6)	4205.4(7)
$Z$	2	4
Density (calc., $\text{g cm}^{-3}$ )	1.183	1.034
Absorption coefficient $\mu$ ( $\text{mm}^{-1}$ )	0.148	0.119
$F(000)$	1172	1376
$\theta$ range for data collection (°)	1.76–25.03	1.62–24.97
Index ranges	$-13 < h < 9, -23 < k < 23, -14 < l < 14$	$0 < h < 15, 0 < k < 21, -21 < l < 21$
Reflections collected	11051	7897
Independent reflections	8211 [ $R(\text{int}) = 0.0340$ ]	7375 [ $R(\text{int}) = 0.0159$ ]
Data/restraints/parameters	8211/1/634	7338/0/457
Goodness of fit on $F^2$	0.477	0.898
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0483, wR_2 = 0.1108$	$R_1 = 0.0846, wR_2 = 0.1985$
$R$ indices (all data)	$R_1 = 0.0860, wR_2 = 0.1546$	$R_1 = 0.2128, wR_2 = 0.3008$
Largest diff. peak and hole ( $\text{e} \text{ \AA}^{-3}$ )	0.249 and $-0.167$	0.463 and $-0.255$

<sup>a</sup> Details in common: crystal system, monoclinic; Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å; temperature 293(2) K; refinement method, full-matrix least-squares on  $F^2$ .

Table 3

Atomic coordinates ( $\times 10^4$ ) for **3** with equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Si(1)	10114(1)	7904(1)	7052(1)	52(1)
Si(2)	7619(1)	8366(1)	6811(1)	57(1)
Si(3)	8459(1)	8249(1)	2428(1)	51(1)
Si(4)	5936(1)	8658(1)	2115(1)	47(1)
O(1)	9925(3)	7789(2)	5797(3)	56(1)
O(2)	8911(3)	8106(2)	7371(3)	67(1)
O(3)	7311(3)	8315(2)	5520(3)	51(1)
O(4)	8719(3)	8301(2)	3726(3)	49(1)
O(5)	7165(3)	8483(2)	1820(3)	59(1)
O(6)	6070(3)	8731(2)	3378(3)	51(1)
C(1)	10667(4)	7180(2)	7886(3)	59(2)
C(2)	10063(4)	6932(3)	8603(4)	89(3)
C(3)	10429(5)	6376(3)	9154(4)	128(4)
C(4)	11399(5)	6066(2)	8988(4)	96(3)
C(5)	12004(4)	6314(2)	8271(4)	90(2)
C(6)	11638(4)	6870(2)	7720(4)	77(2)
C(7)	11160(3)	8583(2)	7501(3)	56(2)
C(8)	12245(4)	8527(2)	8205(4)	83(2)
C(9)	12965(4)	9048(3)	8436(4)	103(3)
C(10)	12600(6)	9626(3)	7963(5)	132(4)
C(11)	11515(6)	9682(2)	7259(5)	137(4)
C(12)	10795(4)	9161(3)	7028(4)	103(3)
C(13)	7553(5)	9206(2)	7262(4)	70(2)
C(14)	6686(4)	9608(4)	6718(4)	108(3)
C(15)	6675(7)	10232(3)	7041(7)	144(5)
C(16)	7531(9)	10455(2)	7907(8)	153(5)
C(17)	8397(7)	10052(4)	8451(6)	196(7)
C(18)	8408(4)	9428(4)	8128(5)	129(4)
C(19)	6614(4)	7882(3)	7436(3)	66(2)
C(20)	6065(5)	8137(3)	8190(4)	104(3)
C(21)	5339(4)	7765(4)	8638(4)	130(4)
C(22)	5161(4)	7138(3)	8333(5)	137(5)
C(23)	5710(5)	6883(2)	7579(6)	145(4)
C(24)	6437(5)	7255(3)	7130(4)	105(3)
C(25)	8576(4)	7406(2)	1959(4)	64(2)
C(26)	7942(4)	7229(3)	932(4)	89(3)
C(27)	8024(4)	6618(3)	564(4)	103(3)
C(28)	8740(5)	6185(2)	1222(5)	119(3)
C(29)	9375(5)	6362(2)	2249(5)	111(3)
C(30)	9293(4)	6973(2)	2617(3)	83(2)
C(31)	9476(3)	8756(2)	1860(3)	61(2)
C(32)	9965(4)	8538(3)	1036(4)	98(3)
C(33)	10708(5)	8922(4)	631(4)	133(5)
C(34)	10961(4)	9524(3)	1049(6)	150(6)
C(35)	10472(5)	9742(2)	1872(6)	135(4)
C(36)	9729(5)	9358(2)	2278(4)	92(3)
C(37)	5410(4)	9400(2)	1325(3)	52(2)
C(38)	5933(3)	9616(2)	523(4)	73(2)
C(39)	5553(4)	10170(2)	-31(4)	85(2)
C(40)	4651(5)	10508(2)	217(4)	91(2)
C(41)	4128(4)	10291(2)	1019(4)	90(3)
C(42)	4508(4)	9737(2)	1573(3)	71(2)
C(43)	4912(3)	7991(2)	1553(3)	56(2)
C(44)	3763(4)	8095(2)	1027(4)	86(2)
C(45)	3018(3)	7589(3)	723(4)	119(4)
C(46)	3422(6)	6978(3)	944(5)	117(4)
C(47)	4570(6)	6873(2)	1470(5)	112(3)
C(48)	5315(4)	7380(4)	1774(4)	80(2)
Li(1)	10203(8)	8185(5)	4625(7)	54(2)
Li(2)	7598(9)	8832(5)	4275(8)	56(3)
Li(3)	5835(8)	8328(6)	4562(8)	63(3)
Li(4)	8394(9)	7770(6)	4936(8)	56(3)

Table 3 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
N(1)	4136(4)	8206(4)	4652(4)	74(2)
N(2)	1924(4)	8195(3)	4491(4)	69(2)
O(1)	7892(4)	9768(3)	4377(4)	90(2)
O(2)	7815(5)	6837(3)	4846(5)	103(2)
C(49)	3858(7)	7963(9)	5524(8)	257(12)
C(50)	2549(6)	7947(8)	5447(8)	223(10)
C(51)	3662(9)	8792(6)	4561(19)	306(14)
C(52)	2335(8)	8812(5)	4451(17)	282(12)
C(53)	3550(7)	7887(9)	3814(10)	260(12)
C(54)	2214(7)	7870(8)	3642(9)	211(9)
C(55)	8787(8)	10143(4)	5004(9)	120(3)
C(56)	8443(10)	10810(6)	4813(11)	165(5)
C(57)	7194(8)	10813(4)	4323(8)	119(3)
C(58)	6973(9)	10173(4)	3853(9)	124(4)
C(59)	8512(10)	6333(5)	5415(11)	165(5)
C(60)	7739(16)	5826(6)	5428(18)	259(10)
C(61)	6803(11)	6548(9)	4282(12)	208(8)
C(62)	6691(15)	5921(9)	4660(20)	306(15)

*U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

metrically opposite donor atoms, oxygen donor atoms in the case of dioxane and nitrogen in the case of DABCO. The DABCO adduct is then expected to be a chain polymer analogous to compound **2**. However, the DABCO adduct could only be successfully crystallised from toluene/THF solutions, and thus THF is also incorporated in the structure. Fig. 1 depicts the crystal structure of the DABCO/THF adduct  $\{[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot (\text{C}_4\text{H}_8\text{O})]_2(\text{C}_6\text{H}_{12}\text{N}_2)_n\}_n$  (**3**) and selected bond lengths and angles are shown in Table 4. The structure is a chain polymer analogous to **2**, where each dimeric unit is bridged by a DABCO unit through the exocyclic lithium atoms. However, the endocyclic lithiums of the dimeric units are solvated by THF and not, as expected by analogy with **2**, DABCO. For compounds **1**, **2** and **3** there are two distinct coordination environments for lithium in the dimeric unit. The endocyclic lithium atoms are four-coordinate and the exocyclic lithium atoms are three-coordinate (if possible Li...Li interactions are to be ignored). The angles at both types of lithium ion are very similar in all the compounds, but greatly distorted from regular tetrahedral or trigonal planar geometry (see Table 1).

The stoichiometric addition of a solution of 4,4'-bipyridine in toluene to  $[(\text{Ph}_2\text{SiOLi})_2\text{O}]$  in the molar ratio 2:1 resulted in precipitation of a white solid. Recrystallisation from a toluene/THF solution resulted in the 4,4'-bipy/THF adduct of dilithium tetraphenyldisiloxanediolate  $\{[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot (\text{C}_4\text{H}_8\text{O})]_2 \cdot 2(\text{C}_{10}\text{H}_8\text{N}_2)_n\}_n$  (**4**), as shown in Fig. 2 with selected bond lengths and angles shown in Table 6. While the basic skeletal framework of the dimeric dilithiodisiloxanediolate is also seen in **4**, the structure differs from **2** and **3** in a number of ways. In **2** and **3** the dimeric units are connected through the exocyclic lithiums giving chain

Table 4  
Selected bond lengths (Å) and angles (°) for compound 3

Si(1)–O(1)	1.569(4)
Si(1)–O(2)	1.638(4)
Si(2)–O(3)	1.591(4)
Si(2)–O(2)	1.632(4)
Si(3)–O(4)	1.601(4)
Si(3)–O(5)	1.629(4)
Si(4)–O(6)	1.576(4)
Si(4)–O(5)	1.639(3)
O(1)–Li(1)	1.803(10)
O(1)–Li(4)	1.889(11)
O(3)–Li(3)	1.884(11)
O(3)–Li(4)	2.003(11)
O(3)–Li(2)	2.017(11)
O(4)–Li(1)	1.877(10)
O(4)–Li(2)	1.997(10)
O(4)–Li(4)	2.014(10)
O(6)–Li(3)	1.805(10)
O(6)–Li(2)	1.915(11)
Li(1)–N(2)#1	2.100(9)
Li(1)–Li(4)	2.447(13)
Li(1)–Li(2)	3.329(14)
Li(2)–O(1)	2.018(12)
Li(2)–Li(3)	2.462(14)
Li(2)–Li(4)	2.515(13)
Li(3)–N(1)	2.072(10)
Li(3)–Li(4)	3.202(14)
Li(4)–O(2)	2.094(13)
N(2)–Li(1)#2	2.100(9)
O(1)–Si(1)–O(2)	111.6(2)
O(3)–Si(2)–O(2)	112.6(2)
O(4)–Si(3)–O(5)	113.1(2)
O(6)–Si(4)–O(5)	112.0(2)
Si(1)–O(1)–Li(1)	138.6(4)
Si(1)–O(1)–Li(4)	118.2(3)
Li(1)–O(1)–Li(4)	83.0(4)
Si(2)–O(2)–Si(1)	140.7(2)
Si(2)–O(3)–Li(3)	127.6(3)
Si(2)–O(3)–Li(4)	114.1(4)
Li(3)–O(3)–Li(4)	110.9(5)
Si(2)–O(3)–Li(2)	136.4(4)
Li(3)–O(3)–Li(2)	78.2(4)
Li(4)–O(3)–Li(2)	77.5(4)
Si(3)–O(4)–Li(1)	122.5(3)
Si(3)–O(4)–Li(2)	114.5(4)
Li(1)–O(4)–Li(2)	118.4(5)
Si(3)–O(4)–Li(4)	135.7(4)
Li(1)–O(4)–Li(4)	77.8(4)
Li(2)–O(4)–Li(4)	77.6(4)
Si(3)–O(5)–Si(4)	139.4(2)
Si(4)–O(6)–Li(3)	142.9(5)
Si(4)–O(6)–Li(2)	117.6(3)
Li(3)–O(6)–Li(2)	82.8(5)
O(1)–Li(1)–O(4)	103.2(4)
O(1)–Li(1)–N(2)#1	116.5(5)
O(4)–Li(1)–N(2)#1	138.3(5)
O(6)–Li(2)–O(4)	110.6(5)
O(6)–Li(2)–O(3)	95.0(4)
O(4)–Li(2)–O(3)	102.5(5)
O(6)–Li(2)–O(1)	106.0(6)
O(4)–Li(2)–O(1)	117.3(5)
O(3)–Li(2)–O(1)	123.1(5)
O(6)–Li(3)–O(3)	103.6(5)
O(6)–Li(3)–N(1)	116.9(6)

Table 4 (continued)

O(3)–Li(3)–N(1)	137.6(5)
O(1)–Li(4)–O(3)	113.2(6)
O(1)–Li(4)–O(4)	95.2(4)
O(3)–Li(4)–O(4)	102.4(5)
O(1)–Li(4)–O(2)	108.2(6)
O(3)–Li(4)–O(2)	109.6(5)
O(4)–Li(4)–O(2)	127.6(6)

Symmetry transformations used to generate equivalent atoms: #1  $x + 1, y, z$ ; #2  $x - 1, y, z$ .

polymers with the lithio-oxane ladders lying along the direction of the polymer chains. In **4** the 4,4'-bipy connects exocyclic to endocyclic lithiums in adjacent dimeric units giving a polymer chain wherein the lithio-oxane ladders are perpendicular to the chain direction. This type of connectivity results in a change in geometry at the exocyclic lithiums, where we see additional binding of THF and an increase in the coordination number to four. The connectivity seen in **4** might result in unfavourable steric interactions between the phenyl groups attached to silicon in neighbouring disiloxanediolate fragments, if the Lewis base were dioxane or DABCO, since in these molecules the linear distances between donor atoms is considerably less than in 4,4'-bipy.

The observed chain structure in **4** consists of 22-membered, rectangular-shaped, monocyclic, dipyriddy-containing rings separated by the dimeric dilithiodisiloxanediolate frameworks. The dipyriddy groups are arranged so that their  $\pi$ -systems are facing each other, forming a wall on either side of the 22-membered rectangular ring. The six-membered lithiosiloxane rings extend above and below opposite sides of the walled rectangle creating a rectangular cavity within the 22-membered cyclic unit.

Table 1 compares the molecular structural parameters of the adducts **1**, **2**, **3** and **4**. All four adducts of dilithium tetraphenyldisiloxanediolate have two types of silicon–oxygen bond; Si–O(Si) and Si–O(Li). The Si–O(Si) bonds are invariably longer than the Si–O(Li) bonds, as would be expected, and are similar to Si–O(Si) distances in hexaphenylcyclotrisiloxane [Ph<sub>2</sub>SiO]<sub>3</sub> (average Si–O(Si) bond length 1.640 Å, orthorhombic form; 1.635 Å, triclinic form) [7].

The Li<sub>endo</sub>–Li<sub>endo</sub> [Li(2)–Li(2')] distances are longer than the Li<sub>exo</sub>–Li<sub>endo</sub> [Li(1)–Li(2)] distances for all four compounds. The variations in Li···Li distances are probably due to different steric requirements of the Lewis bases in each case, rather than any change in electron density at or between the various lithium sites. These Li···Li distances appear to be within bonding range, being much shorter than the Li···Li distances in lithium metal (3.04 Å). It is widely accepted that the short Li···Li interactions, particularly in the complexed lithium amides [(H<sub>2</sub>C(CH<sub>2</sub>)<sub>3</sub>NLi)<sub>3</sub>·PMDETA]<sub>2</sub>

and  $[(\text{H}_2\text{C}(\text{CH}_2)_3\text{NLi})_2 \cdot \text{TMEDA}]_2$ , are due to acute angles ( $74\text{--}78^\circ$ ) at the bridging amido N centres [8]. The related angles in the disiloxanediolate adducts **1**, **2**, **3** and **4** are in the range  $74.7\text{--}83.0^\circ$  and it is possible that the magnitude of these angles causes the short Li...Li interactions. The framework Li–O bonds are assumed to be essentially ionic. The average exocyclic

framework Li–O distances are shorter than the endocyclic Li–O distances in all four compounds.

The angles around the silicon atoms are close to the tetrahedral value of  $109.5^\circ$  for all the compounds. The Si–O–Si angles in these adducts are significantly larger than those found in  $[\text{Ph}_2\text{SiO}]_3$  (average Si–O–Si angles  $131.0^\circ$ , orthorhombic form;  $132.0^\circ$ , triclinic form) [7].

The six-membered  $\text{LiO}_3\text{Si}_2$  planes in all four adducts show significant deviations from planarity (maximum atomic deviations of mean planes are 0.356, 0.436, 0.276 and  $0.302 \text{ \AA}$  for **1**, **2**, **3** and **4** respectively). The maximum deviation from the mean plane in  $[\text{Ph}_2\text{SiO}]_3$  is  $0.07 \text{ \AA}$ .

Table 5

Atomic coordinates ( $\times 10^4$ ) for **4** with equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

	x	y	z	$U_{\text{eq}}$
Si(1)	311(1)	6581(1)	540(1)	37(1)
Si(2)	–910(1)	6681(1)	–999(1)	41(1)
O(1)	–346(3)	6924(3)	–183(3)	50(1)
O(2)	451(3)	5696(2)	502(2)	37(1)
O(3)	–853(3)	5810(3)	–1134(2)	41(1)
Li(1)	–244(8)	4708(6)	581(6)	38(3)
Li(2)	–1432(8)	4850(7)	–1200(7)	52(3)
C(1)	1552(3)	7116(3)	577(3)	43(2)
C(2)	2116(4)	7230(3)	1257(2)	61(2)
C(3)	3051(4)	7582(3)	1273(3)	76(3)
C(4)	3422(3)	7820(3)	609(4)	86(3)
C(5)	2858(4)	7707(3)	–72(3)	86(3)
C(6)	1923(4)	7355(3)	–87(2)	66(2)
C(7)	–363(4)	6892(3)	1377(3)	49(2)
C(8)	–667(5)	7640(3)	1407(4)	92(3)
C(9)	–1230(5)	7882(4)	1983(5)	135(6)
C(10)	–1489(4)	7375(5)	2528(4)	129(6)
C(11)	–1185(5)	6626(5)	2497(3)	124(5)
C(12)	–622(5)	6385(3)	1921(3)	71(3)
C(13)	–269(4)	7232(3)	–1735(3)	55(2)
C(14)	264(4)	6859(3)	–2260(3)	68(3)
C(15)	764(4)	7269(5)	–2777(3)	102(4)
C(16)	732(5)	8053(5)	–2770(4)	124(5)
C(17)	199(6)	8426(3)	–2245(5)	131(5)
C(18)	–301(5)	8015(3)	–1727(4)	97(3)
C(19)	–2243(3)	7070(3)	–977(3)	51(2)
C(20)	–2622(4)	7255(3)	–300(3)	71(3)
C(21)	–3615(4)	7495(4)	–288(3)	91(3)
C(22)	–4229(3)	7551(4)	–953(4)	91(3)
C(23)	–3850(3)	7366(3)	–1630(3)	79(3)
C(24)	–2857(4)	7126(3)	–1642(3)	63(2)
C(25)	–6461(5)	4267(5)	9284(4)	54(2)
C(26)	5410(5)	4304(4)	9290(4)	49(2)
C(27)	4886(5)	4874(4)	8914(4)	44(2)
C(28)	5438(6)	5374(5)	8536(6)	80(3)
C(29)	6476(6)	5300(5)	8545(6)	90(3)
N(1)	6996(4)	4748(4)	8919(4)	59(2)
C(30)	2205(5)	4591(5)	9348(4)	56(2)
C(31)	3207(5)	4454(4)	9296(4)	52(2)
C(32)	3773(4)	4969(4)	8937(4)	39(2)
C(33)	3277(6)	5580(5)	8640(5)	75(3)
C(34)	2255(5)	5654(6)	8715(5)	79(3)
N(2)	1714(4)	5192(4)	9070(3)	47(2)
O(4)	–1615(5)	4648(4)	–2340(4)	94(2)
C(01)	–2288(11)	4164(9)	–2745(8)	148(5)
C(02)	–2408(20)	4532(14)	–3500(14)	297(13)
C(03)	–1974(22)	5121(15)	–3424(18)	377(18)
C(04)	–1308(14)	5187(10)	–2844(10)	183(7)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

### 3. Experimental

All manipulations were carried out in an atmosphere of purified nitrogen using standard Schlenk techniques. Infrared spectra were run on the Perkin-Elmer 1720X spectrometer in the range  $4000\text{--}200 \text{ cm}^{-1}$ , samples were examined as Nujol mulls between caesium iodide plates. Melting-points were determined in nitrogen-filled glass capillary tubes using a Gallenkamp melting-point apparatus. Elemental analyses (carbon, hydrogen and nitrogen) were obtained from the Microanalytical Laboratory at University College, London. Compound **4** gave elemental analyses which were consistently lower for carbon (around 10%) than expected.

1,4-Diazobicyclo[2.2.2]octane and 4,4'-bipyridine were purchased from Aldrich and used as obtained.

#### 3.1. Preparations

$\{[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot (\text{C}_4\text{H}_8\text{O})]_2(\text{C}_6\text{H}_{12}\text{N}_2)\}_n$  (**3**). A solution of *n*-butyllithium ( $6.0 \text{ cm}^3$  of  $2.84 \text{ mol dm}^{-3}$  in hexane,  $0.017 \text{ mol}$ ) was added dropwise to a solution of  $[(\text{Ph}_2\text{SiOH})_2\text{O}]$  ( $3.53 \text{ g}$ ,  $8.51 \text{ mmol}$ ) in toluene (approximately  $20 \text{ cm}^3$ ) at  $0^\circ\text{C}$  and the mixture stirred for 3 h. To this solution was added a solution of DABCO ( $1.91 \text{ g}$ ,  $0.017 \text{ mol}$ ) in toluene (approximately  $15 \text{ cm}^3$ ) dropwise at  $0^\circ\text{C}$  with stirring. A white precipitate formed immediately which was insoluble in hot toluene. A few drops of THF were added and a clear colourless solution resulted. It was then concentrated to around  $20 \text{ cm}^3$  and colourless square crystals of **3** formed at room temperature. Yield  $3.32 \text{ g}$  (35%), m.p.  $249^\circ\text{C}$  (decomp.). Anal. Found: C, 65.19; H, 6.34; N, 2.72%.  $\text{C}_{62}\text{H}_{68}\text{Li}_4\text{N}_2\text{O}_8\text{Si}_4$  Calc.: C, 67.13; H, 6.18; N, 2.53%. IR (Nujol)  $1588(\text{w})$ ,  $1566(\text{w})$ ,  $1319(\text{m})$ ,  $1262(\text{m})$ ,  $1160(\text{w})$ ,  $1115(\text{s})$ ,  $1062(\text{m})$ ,  $1030(\text{s})$ ,  $1013(\text{s})$ ,  $980(\text{s})$ ,  $965(\text{s})$ ,  $925(\text{m})$ ,  $890(\text{sh})$ ,  $860(\text{w})$ ,  $835(\text{w})$ ,  $784(\text{m})$ ,  $740(\text{s})$ ,  $700(\text{s})$ ,  $681(\text{w})$ ,  $621(\text{w})$ ,  $588(\text{w})$ ,  $535(\text{vs})$ ,  $510(\text{m})$ ,  $486(\text{m})$ ,  $439(\text{m})$ ,  $311(\text{s})$ ,  $298(\text{sh})$ ,  $270(\text{w}) \text{ cm}^{-1}$ .

$\{[(\text{Ph}_2\text{SiOLi})_2\text{O} \cdot (\text{C}_4\text{H}_8\text{O})]_2 \cdot 2(\text{C}_{10}\text{H}_8\text{N}_2)\}_n$  (**4**). A

Table 6  
Selected bond lengths (Å) and angles (°) for **4**

Si(1)–O(2)	1.588(3)
Si(1)–O(1)	1.625(3)
Si(1)–C(7)	1.898(3)
Si(1)–C(1)	1.900(3)
Si(2)–O(3)	1.567(3)
Si(2)–O(1)	1.637(3)
Si(2)–C(13)	1.890(3)
Si(2)–C(19)	1.907(3)
O(2)–Li(1)	1.983(8)
O(2)–Li(2)#1	1.992(8)
O(2)–Li(1)#1	2.050(8)
O(3)–Li(2)	1.892(9)
O(3)–Li(1)#1	1.923(8)
Li(1)–O(3)#1	1.923(8)
Li(1)–O(2)#1	2.050(8)
Li(1)–N(2)#2	2.114(8)
Li(1)–Li(1)#1	2.45(2)
Li(1)–Li(2)#1	2.549(10)
Li(1)–Li(2)	3.447(11)
Li(2)–O(2)#1	1.992(8)
Li(2)–O(4)	2.084(10)
Li(2)–N(1)#3	2.108(9)
Li(2)–Li(1)#1	2.549(10)
C(25)–N(1)	1.310(7)
C(25)–C(26)	1.388(7)
C(26)–C(27)	1.356(7)
C(27)–C(28)	1.364(8)
C(27)–C(32)	1.493(6)
C(28)–C(29)	1.390(8)
C(29)–N(1)	1.319(8)
N(1)–Li(2)#4	2.108(9)
C(30)–N(2)	1.307(7)
C(30)–C(31)	1.375(7)
C(31)–C(32)	1.371(7)
C(32)–C(33)	1.373(7)
C(33)–C(34)	1.396(7)
Si(1)–O(2)	1.588(3)
Si(1)–O(1)	1.625(3)
Si(2)–O(3)	1.567(3)
Si(2)–O(1)	1.637(3)
O(2)–Li(1)	1.983(8)
O(2)–Li(2)#1	1.992(8)
O(2)–Li(1)#1	2.050(8)
O(3)–Li(2)	1.892(9)
O(3)–Li(1)#1	1.923(8)
Li(1)–O(3)#1	1.923(8)
Li(1)–O(2)#1	2.050(8)
Li(1)–N(2)#2	2.114(8)
Li(1)–Li(1)#1	2.45(2)
Li(1)–Li(2)#1	2.549(10)
Li(1)–Li(2)	3.447(11)
Li(2)–O(2)#1	1.992(8)
Li(2)–O(4)	2.084(10)
Li(2)–N(1)#3	2.108(9)
Li(2)–Li(1)#1	2.549(10)
N(1)–Li(2)#4	2.108(9)
N(2)–Li(1)#2	2.114(8)
O(3)–Si(2)–O(1)	111.7(2)
Si(1)–O(1)–Si(2)	141.9(2)
Si(1)–O(2)–Li(1)	144.6(3)
Si(1)–O(2)–Li(2)#1	121.1(3)
Li(1)–O(2)–Li(2)#1	79.8(3)
Si(1)–O(2)–Li(1)#1	112.5(3)

Table 6 (continued)

Li(1)–O(2)–Li(1)#1	74.7(4)
Li(2)#1–O(2)–Li(1)#1	117.0(4)
Si(2)–O(3)–Li(2)	151.4(3)
Si(2)–O(3)–Li(1)#1	116.1(3)
Li(2)–O(3)–Li(1)#1	83.9(3)
O(3)#1–Li(1)–O(2)	97.2(3)
O(3)#1–Li(1)–O(2)#1	110.7(4)
O(2)–Li(1)–O(2)#1	105.3(4)
O(3)#1–Li(1)–N(2)#2	124.8(4)
O(2)–Li(1)–N(2)#2	112.9(4)
O(2)#1–Li(1)–N(2)#2	104.6(3)
O(3)–Li(2)–O(2)#1	98.0(4)
O(3)–Li(2)–O(4)	102.9(4)
O(2)#1–Li(2)–O(4)	123.9(5)
O(3)–Li(2)–N(1)#3	118.9(5)
O(2)#1–Li(2)–N(1)#3	120.8(5)
O(4)–Li(2)–N(1)#3	92.8(4)

Symmetry transformations used to generate equivalent atoms: #1  $-x, y+1, -z$ ; #2  $-x, -y+1, +z+1$ ; #3  $x-1, y, z-1$ ; #4  $x+1, y, z+1$ .

solution of  $[(\text{Ph}_2\text{SiOH})_2\text{O}]$  (2.35 g, 5.67 mmol) in toluene (approximately 15 cm<sup>3</sup>) was treated with a solution of *n*-butyllithium (4 cm<sup>3</sup> of 2.84 mol dm<sup>-3</sup> in hexane) at 0°C. After stirring for 3 h a solution of 4,4'-bipyridine (1.77 g, 0.011 mol) in toluene (approximately 10 cm<sup>3</sup>) was added dropwise with stirring. A white precipitate formed immediately which did not dissolve in hot toluene. However, on addition of a few drops of THF, a clear colourless solution was obtained. This solution as concentrated to around 20 cm<sup>3</sup> and colourless crystals of **4** separated at room temperature. Yield 2.68 g, (36%), m.p. 128°C (soft.), 225°C (decomp.). IR (Nujol) 1598(m), 1535(w), 1262(m), 1200(w), 1154(w), 1113(s), 1090(w), 1043(s), 1014(s), 997(m), 975(s), 917(w), 806(s), 740(m), 707(vs), 690(w), 620(m), 530(s), 493(m), 425(w), 398(w), 314(m), 228(m) cm<sup>-1</sup>.

### 3.2. X-ray crystallography

Single crystals were mounted in 0.7 mm glass capillaries (Lindemann tubes) and sealed under argon. Data were recorded with a CAD4 diffractometer operating in the  $\omega/2\theta$  scan mode. The structures were solved by standard heavy-atom techniques and refined by least-squares [9] with phenyl groups treated as rigid hexagons [ $\text{C}-\text{C}$  1.393 Å,  $\text{C}-\text{C}-\text{C}$  120°] and with inclusion of hydrogen atoms at fixed positions ( $\text{C}-\text{H}$  0.96 Å). The carbons of the THF rings in **4** were disordered. The occupancy factors for the disordered positions were refined and then fixed to allow for anisotropic refinement. No attempt was made to locate or fix hydrogen positions. Crystal data for **3** and **4** are collated in Table 2. Atom coordinates and selected bond lengths and angles for **3** are given in Tables 3 and 4 respectively. For compound **4**, atom coordinates and bond lengths

and angles are given in Tables 5 and 6 respectively. Tables of thermal parameters and H atom coordinates and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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