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Synthesis and structure of the unusual dimeric lithium derivative of the tetraphenyldisiloxanediolate dianion

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Abstract

The synthesis and structure of the new compound bis[dipyridinodilithium tetraphenyldisiloxanediolate], $[Ph_4Si_2O(OLiPy)_2]_2$ (**1**), are described, and a number of unusual features discussed.

Introduction

We recently reported on the reaction between dilithium tetraphenyldisiloxanediolate $Ph_4Si_2O(OLi)_2$ (**A**) and $TiCl_4$, in which an expanded siloxane chain was incorporated into the product to give the titanatrisiloxane *cis*-$Py_2Ti(OSiPh_2(OSiPh_2)_2O)_2$ [1]. We have now isolated the pyridine complex of **A**, confirming our previous conclusion that this reagent is formed with the disiloxane intact from the disiloxanediol and methyllithium. The pyridine adduct of **A** has now been shown by an X-ray diffraction study to have the unusual dimeric molecular structure shown in Fig. 1.

Experimental

A solution of tetraphenyldisiloxanediol $Ph_4Si_2(OH)_2$ (4.0 g, 9.65 mmol) in tetrahydrofuran (30 cm^3) was treated dropwise with a solution of methyllithium (8.4 cm^3 of 2.3 mol dm^{-3} solution in diethyl ether, 19.3 mmol). The mixture was stirred for 3 h and the ethers were then evaporated off, the residue was extracted with toluene, and the filtered extract was concentrated to ca. 25 cm^3. Pyridine was added to the point of turbidity, and colourless crystals of the product **1** separated. 1.8 g (32%); m.p. 376 °C. Found: C, 69.67; H, 5.09; N, 3.65. $C_{34}H_{30}O_3Si_2N_2Li_2$ calcd.: C, 69.84; H, 5.18; N, 4.79%. ^{7}Li NMR (C_6D_6), −2.19(s), ^{7}Li NMR (solid), 1.99(s).

Crystal data for 1. $C_{34}H_{30}Li_2O_3N_2Si_2$, $M = 584.677$, triclinic, a 11.183(4), b 13.458(4), c 13.377(5) Å, α 115.87(3), β 13.458(4), γ 101.53(3)°, U 1640.35 Å^3, space

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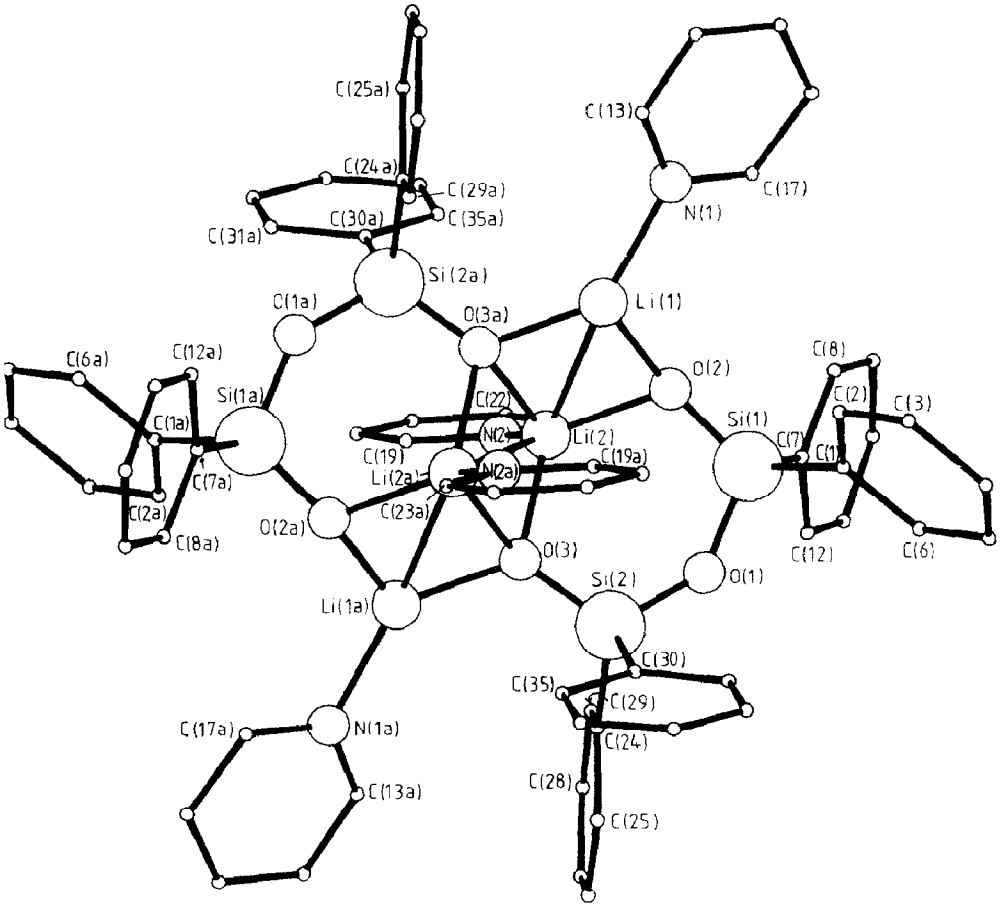

Fig. 1. X-ray crystal structure of $[PyLiOSiPh_2OSiPh_2OLiPy]_2$ (1) (phenyl and pyridine carbon atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Li(1)–O(2) 1.800(8), Li(1)–O(3a) 1.874(7), Li(1)–N(1) 2.049(8), Li(1)–Li(2) 2.472(11), Li(2)–O(2) 1.943(7), Li(2)–O(3) 2.011(7), Li(2)–O(3a) 1.992(8), Li(2)–N(2) 1.992(8), Si(1)–O(1) 1.644(3), Si(1)–O(2) 1.573(3), Li(2)–Li(2a) 2.506(6), O(2)–Li(1)–O(3a) 102.93(3), O(2)–Li(2)–O(3) 111.53(4), O(2)–Si(1)–O(1) 111.88(2), Li(1)–O(2)–Li(2) 82.59(3), Li(2)–O(3)–Li(1a) 116.82(2), Si(1)–O(1)–Si(2) 138.86(2).

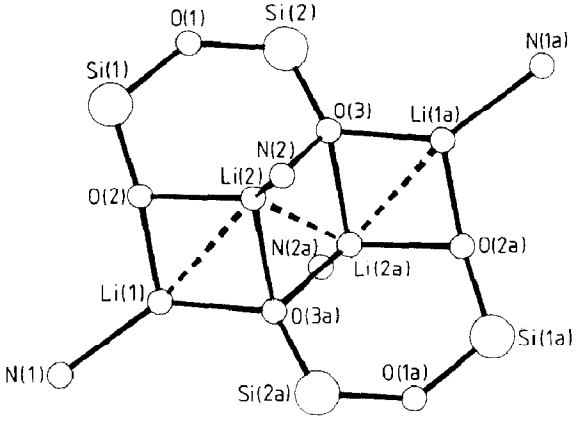

Fig. 2. Structural formula of the essential core in 1.

group $P\bar{1}$, $Z = 2$, D_c 1.184 g cm^{-3}, (Mo–K_α) 0.71069 Å, μ 1.370 cm^{-1}. Data recorded with CAD4 diffractometer in ω–2θ scan mode; 5758 unique reflections measured, 4098 observed with [$F > 3\sigma F_o$]. The structure was solved by direct methods, refined by least squares [phenyl groups treated as rigid hexagons (C–C 1.395 Å) with inclusion of hydrogen atoms at fixed distance (C–H 0.96 Å)] to

Table 1

Fractional atomic coordinates ($\times 10^4$) for $C_{34}H_{30}Li_2N_2O_3Si_2$.

Atoms	x	y	z
Si(1)	753(2)	3153(1)	6400(1)
Si(2)	217(1)	1351(1)	3782(1)
Li(1)	−368(9)	1113(8)	7037(8)
Li(2)	1000(8)	865(7)	5790(7)
N(1)	9182(5)	1782(4)	8557(4)
N(2)	7087(5)	−921(5)	3827(4)
O(1)	731(3)	2621(3)	5018(3)
O(2)	508(4)	2171(3)	6746(3)
O(3)	213(3)	291(3)	4025(3)
C(2)	−1641(4)	3495(3)	6664(4)
C(3)	−2599(4)	4015(3)	6621(4)
C(4)	−2431(4)	4934(3)	6380(4)
C(5)	−1306(4)	5333(3)	6183(4)
C(6)	−348(4)	4813(3)	6227(4)
C(1)	−516(4)	3894(3)	6468(4)
C(8)	2850(5)	4829(4)	8597(4)
C(9)	4111(5)	5648(4)	9318(4)
C(10)	4953(5)	5953(4)	8793(4)
C(11)	4535(5)	5439(4)	7546(4)
C(12)	3274(5)	4619(4)	6824(4)
C(7)	2432(5)	4314(4)	7350(4)
C(13)	8393(6)	1238(6)	8901(6)
C(14)	8139(7)	1777(7)	9919(6)
C(15)	8726(11)	2919(8)	10637(7)
C(16)	9547(13)	3504(8)	10334(8)
C(17)	9753(10)	2911(6)	9279(7)
C(18)	6945(8)	120(7)	4304(7)
C(19)	4186(11)	−332(11)	5900(9)
C(20)	4721(11)	−625(14)	3317(10)
C(21)	4779(10)	−1724(11)	2789(9)
C(22)	6009(8)	−1844(8)	3070(7)
C(24)	914(3)	1392(3)	1847(3)
C(25)	1790(3)	1555(3)	1292(3)
C(26)	3131(3)	1885(3)	1890(3)
C(27)	3596(3)	2051(3)	3043(3)
C(28)	2720(3)	1887(3)	3598(3)
C(23)	1379(3)	1558(3)	3000(3)
C(30)	−1904(3)	2078(2)	3093(3)
C(31)	−3182(3)	1902(2)	2448(3)
C(32)	−4030(3)	770(2)	1554(3)
C(33)	−3600(3)	−186(2)	1306(3)
C(34)	−2322(3)	−10(2)	1951(3)
C(29)	−1474(3)	1122(2)	2845(3)

Table 2

Bond lengths (Å) and angles (°) for $C_{34}H_{30}Li_2N_2O_3Si_2$.

Bond lengths			
O(1)–Si(1)	1.644(5)	O(2)–Si(1)	1.573(5)
C(1)–Si(1)	1.888(6)	C(7)–Si(1)	1.885(7)
O(1)–Si(2)	1.632(5)	O(3)–Si(2)	1.593(5)
C(23)–Si(2)	1.893(6)	C(29)–Si(2)	1.884(6)
Li(1)–Li(2)	2.472(11)	Li(1)–O(2)	1.800(8)
Li(1)–N(1)	2.049(8)	Li(1)–O(3a)	1.874(7)
Li(2)–N(2)	2.057(8)	Li(2)–Li(2a)	2.506(8)
Li(2)–O(2)	1.943(7)	Li(2)–O(3a)	1.992(7)
Li(2)–O(3)	2.011(7)	C(17)–N(1)	1.300(9)
C(13)–N(1)	1.323(8)	C(22)–N(2)	1.322(9)
C(18)–N(2)	1.323(9)	C(15)–C(14)	1.315(11)
C(14)–C(13)	1.357(9)	C(17)–C(16)	1.379(12)
C(16)–C(15)	1.337(13)	C(22)–C(21)	1.399(13)
C(21)–C(20)	1.357(14)		
Bond angles			
O(2)–Si(1)–O(1)	111.9(3)	C(1)–Si(1)–O(1)	105.4(3)
C(1)–Si(1)–O(2)	113.7(3)	C(7)–Si(1)–O(1)	103.9(3)
C(7)–Si(1)–O(2)	112.3(3)	C(7)–Si(1)–C(1)	108.9(3)
O(3)–Si(2)–O(1)	112.8(3)	C(23)–Si(2)–O(1)	103.9(3)
C(23)–Si(2)–O(3)	112.4(3)	C(29)–Si(2)–O(1)	107.6(3)
C(29)–Si(2)–O(3)	111.2(3)	C(29)–Si(2)–C(23)	108.5(3)
O(2)–Li(1)–O(3a)	102.93(4)	Li(2)–Li(1)–N(1)	157.88(5)
N(1)–Li(1)–O(3a)	138.72(5)	N(1)–Li(1)–O(2)	116.31(5)
O(2)–Li(2)–O(3)	111.53(4)	N(2)–Li(2)–O(3)	107.80(6)
O(2)–Li(2)–O(3a)	93.88(6)	N(2)–Li(2)–O(3a)	116.59(7)
N(2)–Li(2)–O(2)	122.49(6)	C(22)–N(2)–C(18)	116.7(8)
C(17)–N(1)–C(13)	115.6(7)	C(1)–C(2)–C(3)	120.0
Si(2)–O(1)–Si(1)	138.2(2)		

$R = 0.06231$, $R_w = 0.0574$ for 384 parameters. The complete structure is shown in Fig. 1, and that of the essential core in Fig. 2. Atomic coordinates are given in Table 1 and bond lengths and angles in Table 2. Lists of thermal parameters and final structure factors are available from the authors.

Discussion

Compound **1** is based on a 12-membered $Li_2Si_4O_6$ ring. This pentacyclic system is to some extent related to that in the mineral thortveitite $[Sc_2Si_2O_7]$ [2], which may be viewed as an extended series of interconnecting overlapping 12-membered $Sc_2Si_4O_6$ rings with Si_2O_2 bridges. The most striking features of **1** involve the three 4-membered lithiooxane rings. These have a folded ladder arrangement similar to that found in the polymeric compound $[Ph_2CH_2SLiPy]_\infty$ [3]. However, in the present case the Li ··· Li distances appear to be within bonding range (e.g. Li(1)–Li(2) 2.479 Å and Li(2)–Li(2a) 2.465 Å), being much shorter than Li ··· Li distances in metallic lithium (3.04 Å) and in gaseous lithium (2.67Å) but close to those reported as within bonding range in the cluster $(LiC_6H_4CH_2 \cdot NLi \cdot CH_2CH_2NMe_2)_4$ [4]. It is noteworthy that only a single resonance was observed in

both the solution and solid state ^{7}Li NMR spectra despite apparent presence of two coordination environments and Li · · · Li interactions.

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