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Crystal and molecular structures of hexameric lithium dimethylnaphthylsilanolate, $[\mathrm{LiOSiNpMe_2}]_6$ *

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Abstract

In the solid lithium dimethyl(naphthylsilanolate) exists as hexamer $[\mathrm{LiOSiNpMe_2}]_6$ containing a puckered $\mathrm{Li_6}$ ring with bridging O atoms bound to tetrahedral silicon centres.

Introduction

During a study of the reaction of α-naphthyllithium with iron trichloride in ether solution with the objective of isolating iron complexes which would react with dinitrogen [1–3] we isolated from the products a compound which turned out, unexpectedly, to be lithium dimethylnaphthylsilanolate $[\mathrm{LiOSiNpMe_2}]$. The only source of silicon in the system was the silicone grease (supplied by the Rhônc Poulenc Co.) used on the glass joints. The grease contains the polymer $[\mathrm{Me_2SiO}]_n$, which is readily soluble in ether. Presumably the grease was partially dissolved in ether and then treated with α-naphthyllithium to form I:

$$[\mathrm{Me_2SiO}]_n + n\mathrm{LiNp} \rightarrow \underset{\text{(I)}}{n[\mathrm{LiOSiMe_2Np}]}$$

This type of reaction was used to prepare lithium trimethylsilanolate from methyllithium [4], and compounds of the general formula $[\mathrm{LiOSiR_3}]$ are known for R = Me, Ph, $\mathrm{PhCH_2}$ [5]. As described below, an X-ray study of single crystals of I showed it to be a hexamer, in which there are LiLi bonds, a feature previously unknown for organolithium compounds containing Li–O bonds.

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* Dedicated to Professor Luigi Sacconi in recognition of his important contributions to organometallic chemistry.

Experimental

The ethereal product mixture was evaporated and the residue extracted with pentane. Single crystals of I formed in the pentane solution on long standing at

Table 1

Coordinates ($\times 10^4$) of Si, O, Li, C atoms, with their thermal parameters, (B [a], Å^2)

Atom	x	y	z	B
Si	4504(2)	4023(1)	2406(2)	3.9
O	4855(3)	4355(2)	3589(3)	3.5
Li	5087(11)	5167(5)	3368(12)	4.1
C(1)	3159(5)	3664(3)	2499(6)	4.3
C(2)	2420(7)	3804(3)	1710(7)	5.9
C(3)	1384(7)	3519(4)	1788(8)	6.8
C(4)	1095(7)	3177(4)	2644(8)	7.0
C(5)	1727(6)	3011(7)	3461(7)	5.3
C(6)	1409(7)	2630(4)	4388(8)	6.7
C(7)	2050(8)	2502(4)	5143(8)	7.7
C(8)	3096(8)	2701(4)	5112(8)	7.3
C(9)	3447(6)	3091(3)	4223(6)	4.9
C(10)	2793(6)	3258(3)	3389(6)	4.6
C(11)	5287(7)	3471(4)	2022(7)	7.2
C(12)	4603(7)	4580(4)	1218(7)	6.6
Si′	3875(2)	6187(1)	3340(2)	4.1
O′	4414(4)	5727(2)	4044(4)	4.2
Li′	4307(10)	4180(5)	5076(10)	4.2
C(1′)	2537(7)	5857(3)	2942(6)	3.5
C(2′)	2255(7)	5267(3)	3144(6)	4.1
C(3′)	1283(7)	4979(4)	2835(7)	4.9
C(4′)	610(7)	5266(4)	2295(8)	5.2
C(5′)	860(7)	5862(4)	2060(7)	4.7
C(6′)	162(7)	6172(4)	1520(8)	6.3
C(7′)	387(8)	6731(4)	1275(9)	6.3
C(8′)	1321(9)	7038(4)	1621(9)	6.4
C(9′)	2034(7)	6754(4)	2150(7)	4.4
C(10′)	1829(7)	6158(3)	2377(7)	3.8
C(11′)	4532(8)	6398(4)	1944(9)	6.8
C(12′)	3888(9)	6843(5)	4241(9)	6.6
Si″	2565(2)	4404(1)	6704(2)	3.9
O″	3578(3)	4638(2)	5979(4)	3.7
Li″	3905(11)	5437(6)	5523(11)	4.6
C(1″)	2297(6)	5010(3)	7681(7)	4.3
C(2″)	2396(6)	4956(3)	8858(7)	5.4
C(3″)	2255(7)	5401(4)	9652(8)	6.2
C(4″)	2032(7)	5898(4)	9265(8)	6.2
C(5″)	1890(7)	5994(4)	8073(7)	5.5
C(6″)	1618(7)	6509(4)	7663(8)	6.8
C(7″)	1506(8)	6603(4)	6535(9)	7.2
C(8″)	1604(7)	6170(4)	5725(8)	6.6
C(9″)	1873(6)	5652(3)	6092(7)	5.3
C(10″)	2039(6)	5545(3)	7289(6)	4.2
C(11″)	1455(7)	4154(4)	5770(8)	5.8
C(12″)	2743(7)	3778(4)	7633(8)	6.2

[a] Values of B_{eq} are shown for Si and O atoms, and those of B_{iso} for C, and Li atoms.

room temperature. In addition to I, the solution contained residual naphthyllithium and naphthyl derivative of iron formed from FeCl$_3$ [3].

No attempts were made to optimize the synthetic procedure for I or to find out whether the iron compounds had any catalytic effect.

For the diffraction study a single crystal of I was sealed in a glass capillary ($\varnothing$0.07 mm) under argon. The cell dimensions and intensities of 1865 independent reflections with $I \geqslant 2\sigma(I)$ were measured with a 'Syntex P$\bar{1}$' four-circle automatic diffractometer (λ(Mo-K_α)), graphite monochromator, $\theta/2\theta$ scan $(\sin\theta/\lambda)_{\max} = 0.604$. No absorption correction was made.

Table 2

Coordinates ($\times 10^3$) of hydrogen atoms and C–H bond lengths (r, Å)

Atom [a]	x	y	z	r (Å)
H(2)	277(5)	404(3)	111(6)	0.96(7)
H(3)	115(5)	383(3)	167(6)	0.85(7)
H(4)	31(5)	294(3)	279(6)	1.12(7)
H(6)	52(5)	247(3)	411(6)	1.23(7)
H(7)	186(5)	232(3)	595(6)	1.04(7)
H(8)	364(5)	255(3)	559(6)	1.02(8)
H(9)	432(5)	319(3)	418(6)	1.16(7)
H(11)	525(6)	316(3)	253(6)	0.93(7)
H(11$_1$)	509(6)	338(3)	120(6)	1.00(7)
H(11$_2$)	598(6)	368(3)	195(6)	0.98(7)
H(12)	413(6)	484(3)	133(6)	0.95(8)
H(12$_1$)	457(5)	428(3)	62(6)	0.98(7)
H(12$_2$)	543(6)	466(3)	109(6)	0.99(7)
H(2′)	274(5)	503(3)	363(6)	1.08(7)
H(3′)	119(5)	455(3)	304(4)	1.01(7)
H(4′)	−7(6)	503(3)	209(6)	1.03(7)
H(6′)	−22(5)	583(3)	126(6)	0.92(6)
H(7′)	−13(6)	697(3)	165(6)	1.06(8)
H(8′)	157(5)	743(3)	153(6)	0.93(7)
H(9′)	270(5)	697(3)	247(6)	1.01(7)
H(11′)	468(6)	604(3)	148(6)	1.05(7)
H(11$'_1$)	413(5)	666(3)	137(6)	1.11(8)
H(11$'_2$)	513(5)	660(3)	230(6)	0.95(7)
H(12′)	355(5)	677(3)	502(6)	1.01(7)
H(12$'_1$)	466(6)	697(3)	440(6)	1.04(8)
H(12$'_2$)	359(6)	710(3)	389(6)	0.87(8)
H(2″)	256(5)	460(3)	909(6)	0.94(7)
H(3″)	234(5)	524(3)	1058(6)	1.04(7)
H(4″)	211(5)	631(3)	988(6)	1.19(7)
H(6″)	164(5)	691(3)	830(6)	1.18(7)
H(7″)	113(5)	697(3)	615(6)	1.16(8)
H(8″)	125(6)	614(3)	499(6)	0.97(7)
H(9″)	188(5)	526(3)	565(6)	1.06(7)
H(11″)	93(5)	439(3)	583(6)	0.97(8)
H(11$''_1$)	146(5)	376(3)	569(6)	0.92(7)
H(11$''_2$)	158(6)	423(3)	505(6)	0.87(7)
H(12″)	315(6)	386(3)	829(6)	0.93(7)
H(12$''_1$)	286(6)	350(3)	718(6)	0.87(7)
H(12$''_2$)	194(6)	364(3)	802(6)	1.17(7)

[a] The numbering of hydrogen atoms corresponds to that of the carbon atoms to which they are attached.

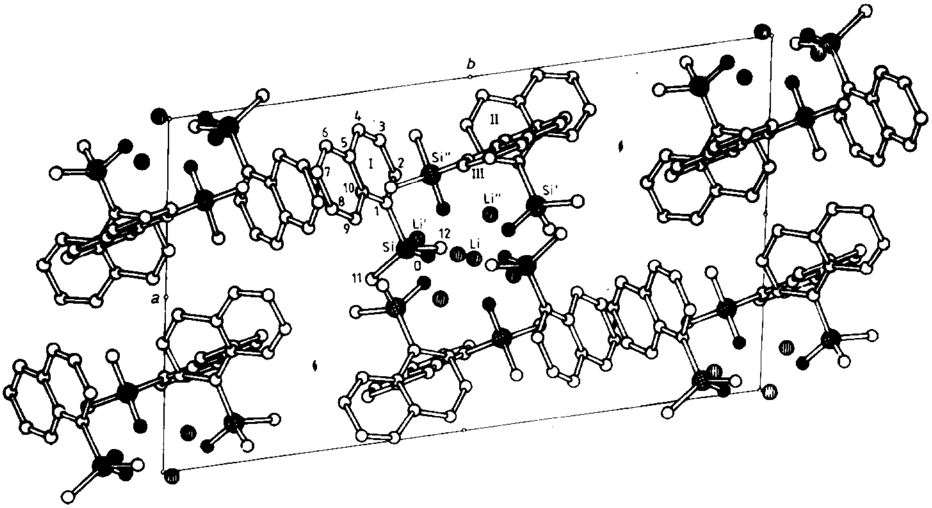

Fig. 1. The structure of the Li(NpSiMe$_2$O)$_6$ complex projected along the c direction.

The structure was solved by the direct method and refined by a least-squares procedure in full matrix anisotropic (for Si and O atoms) and isotropic (for C and Li atoms) approximations. Hydrogen atoms were located from differential synthe-

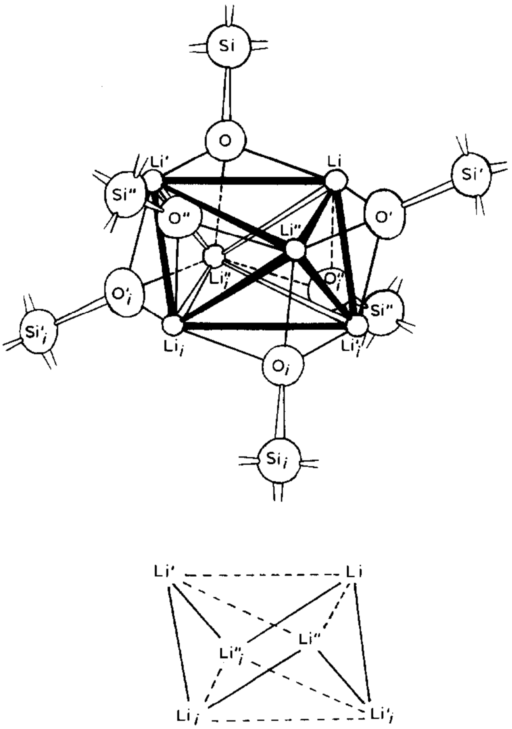

Fig. 2. Li$_6$ hexamer with surrounding O(–Si$\lessdot$) atoms. The Li$_6$ hexamer is shown in the lower part of the figure.

Table 3

Interatomic O–Li and Li$\cdots$Li distances in complex I [a]

Distance	r (Å)
O–Li	1.89(1)
O–Li$'$	1.90(1)
O–Li$_i''$	1.95(1)
O$'$–Li	1.89(1)
O$'$–Li$''$	1.93(1)
O$'$–Li$_i'$	1.98(1)
O$''$–Li$'$	1.89(1)
O$''$–Li$''$	1.92(1)
O$''$–Li$_i$	1.93(1)
Li$\cdots$Li$'$	3.09(2)
Li$\cdots$Li$''$	3.08(2)
Li$'\cdots$Li$''$	3.12(2)
Li$\cdots$Li$_i'$	2.42(2)
Li$\cdots$Li$_i''$	2.48(2)
Li$'\cdots$Li$_i''$	2.52(2)

[a] Symmetry matrix: i $(1-x, 1-y, 1-z)$.

ses, and only their position parameters were refined. Calculations were performed with the Roentgen-75 program [6]. The final R index was 0.067. Coordinates of non-hydrogen atoms and their temperature factors are shown in Table 1, and the coordinates of hydrogen atoms and C–H bond lengths in Table 2.

Results and discussion

The crystals of I were found to be monoclinic, a 13.45(2), b 23.41(7), c 11.59(2) Å, γ 99.5(2)°, V 3597.5 Å^3, $M = 1249.56$, d_{calc} 1.15 g/cm^3, $Z = 2$, space group $P2_1/n$. The structure projection along c direction is shown in Fig. 1. Complex I could conceivably be regarded as a lithium salt of the anion [NpSiMe$_2$O]$^-$, but its structure corresponds to that of known organolithium compounds containing covalent Li–X bonds and forming polymers by Li–Li bonding [7,8]. As shown in Fig. 2, the structure of I consists of a hexameric Li$_6$ ring stabilized by the $\geqslant$OSiMe$_2$Np bridges. The structure of I may be also regarded as a distorted octahedron formed by six lithium atoms, with two opposite facets broadened compared with all the others bridged by oxygen.

The mean LiLi bond length in the puckered Li$_6$ rings is 2.47 Å, indicating strong LiLi bonding (the Li–Li bond length in the Li$_2$ molecule is 2.67 Å). The Li–O and Li–Li bond lengths are shown in Table 3. Si atom in the anionic part of I has a tetrahedral environment with normal values of Si–O and Si–C bond lengths (Table 4) [9]. The structure of I and the Li–Li bond lengths are similar to those for other known hexameric organolithium compounds (see Table 5). Of the known Li$_6$ species [10–13] I contains the most electronegative atom (oxygen) bound to lithium. Like the nitrogen-containing compounds I contains no electron deficient bridges

Table 4

Bond lengths (r, Å) and valency angles (ω, degree) in the anionic part of I

r	I	II	III	ω	I	II	III
Si–O	1.604(4)	1.616(6)	1.615(5)	O–Si–C(1)	110.7(3)	110.8(4)	108.2(3)
Si–C(1)	1.864(8)	1.891(9)	1.897(8)	O–Si–C(11)	112.8(3)	111.7(4)	113.0(4)
Si–C(11)	1.85(1)	1.87(1)	1.86(1)	O–Si–C(12)	107.8(4)	108.9(5)	110.7(4)
Si–C(12)	1.89(1)	1.86(1)	1.87(1)	C(1)–Si–C(11)	108.8(4)	105.7(4)	109.9(4)
C(1)–C(2)	1.43(1)	1.39(1)	1.38(1)	C(1)–Si–C(12)	107.7(4)	110.5(5)	108.0(4)
C(1)–C(10)	1.43(1)	1.43(1)	1.43(1)	C(11)–Si–C(12)	108.9(4)	109.3(5)	106.9(4)
C(2)–C(3)	1.44(1)	1.41(1)	1.43(1)	Si–C(1)–C(2)	121.3(5)	116.5(7)	119.3(6)
C(3)–C(4)	1.29(1)	1.37(1)	1.33(1)	Si–C(1)–C(10)	122.6(6)	125.2(6)	124.7(6)
C(4)–C(5)	1.37(1)	1.40(1)	1.42(1)	C(2)–C(1)–C(10)	116.0(7)	118.1(8)	115.9(7)
C(5)–C(6)	1.42(1)	1.43(1)	1.40(1)	C(1)–C(2)–C(3)	120.6(7)	120.4(8)	123.0(8)
C(5)–C(10)	1.45(1)	1.42(1)	1.43(1)	C(2)–C(3)–C(4)	120.0(9)	121.3(8)	119.9(8)
C(6)–C(7)	1.30(1)	1.32(1)	1.34(1)	C(3)–C(4)–C(5)	124.7(9)	126.0(8)	121.6(9)
C(7)–C(8)	1.41(1)	1.40(1)	1.40(1)	C(4)–C(5)–C(6)	124.6(8)	121.5(8)	121.9(8)
C(8)–C(9)	1.41(1)	1.40(1)	1.39(1)	C(4)–C(5)–C(10)	117.7(7)	118.8(9)	117.7(8)
C(9)–C(10)	1.41(1)	1.40(1)	1.44(1)	C(6)–C(5)–C(10)	117.8(8)	119.7(8)	120.4(8)
				C(5)–C(6)–C(7)	121.0(9)	122.5(9)	121.7(9)
				C(6)–C(7)–C(8)	124.9(9)	118.8(9)	120.6(9)
				C(7)–C(8)–C(9)	116.2(9)	120.8(9)	119.7(9)
				C(8)–C(9)–C(10)	121.9(7)	121.4(8)	121.4(8)
				C(1)–C(10)–C(5)	120.6(7)	120.7(8)	121.8(7)
				C(1)–C(10)–C(9)	121.3(7)	122.6(8)	122.0(7)
				C(5)–C(10)–C(9)	118.1(7)	116.7(8)	116.1(7)

Table 5

Interatomic distances in hexameric organolithium compounds

Compound	Li–Li	Li–X [a]	Ref.
$(LiC_6H_{11})_6$	2.405 2.98	2.184 2.30	10
$(LiSiMe_3)_6$	2.72(2) 3.25(4)	2.68	11,12
$\{Li(N{=}CBu^t_2)\}_6$	2.35(1) 3.21(1)	2.06(1)	13
$\{Li[N{=}C(NMe_2)]\}_6$	2.445(2) 3.166(2)	2.00(1)	13
$(LiOSiNpMe_2)_6$	2.47(2) 3.10(2)	1.92(2)	This work

[a] X = C, Si, N, O.

such as present in, e.g., $[LiC_6H_{11}]_6$. Formation of stable six-membered Li_6 rings is evidently a general feature of lithium compounds with covalent Li–X bonds.

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