An X-ray Crystallographic Study of an Unusual Lithium Silanolate Hexamer, $[LiOSi(Me)_2OC(H)_2SiMe_3]_6$

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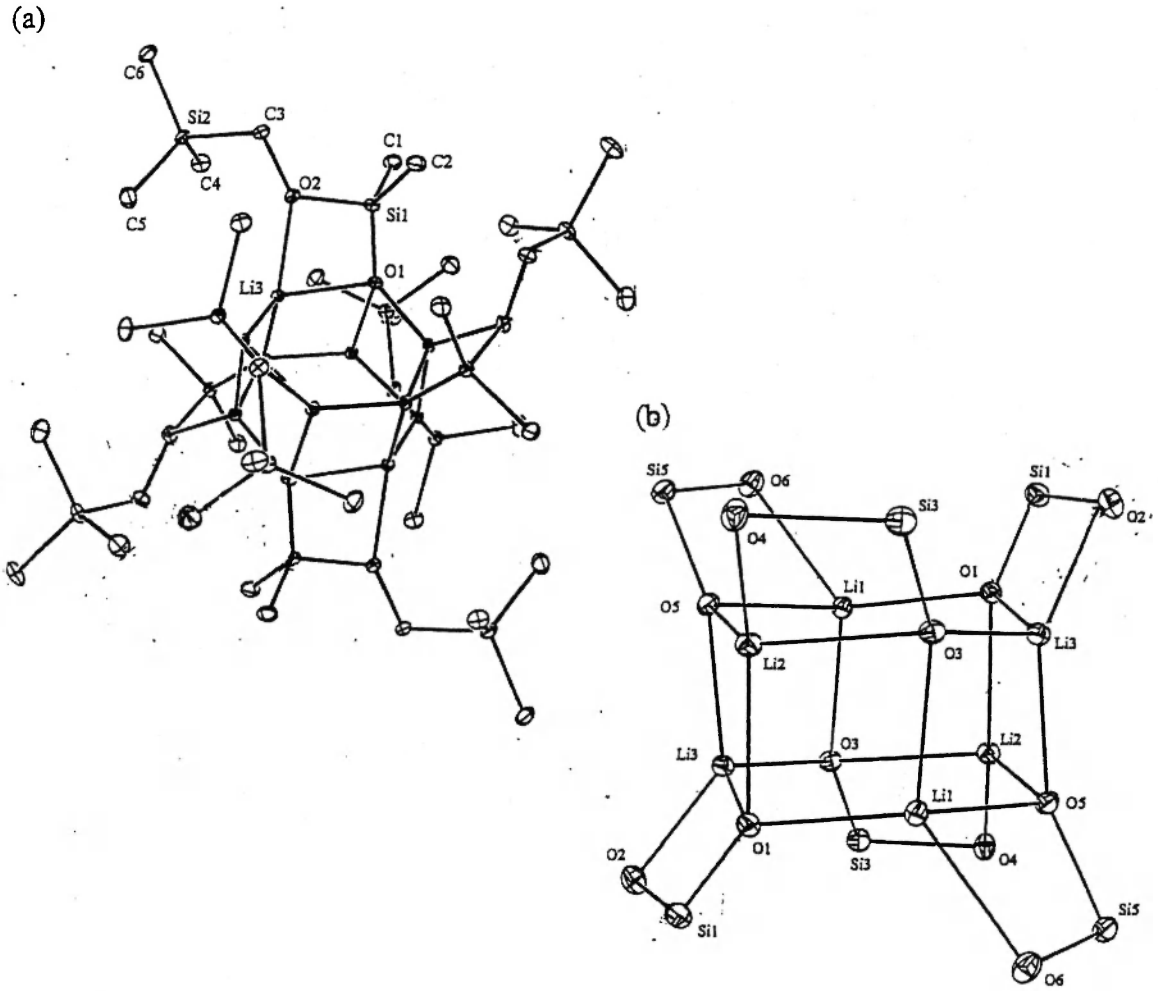
Figure 1. (a) Molecular structure of $[LiOSi(Me)_2OC(H)_2SiMe_3]_6$ **I** showing (b) the coordination geometry of its central Li_6O_6 core (hydrogens omitted for clarity, 20% ellipsoids). Key geometric parameters (Å, °): O(1)-Li(1) 1.891(5), O(1)-Li(2)' 1.924(5), O(1)-Li(3)' 2.098(5), O(2)-Li(3)' 2.024(5), O(3)-Li(3) 1.883(5), O(3)-Li(1) 1.924(5), O(3)-Li(2)' 2.094(5), O(4)-Li(2)' 2.038(5), O(5)-Li(2) 1.889(5), O(5)-Li(3) 1.917(5), O(5)-Li(1) 2.099(6), Si(1)-O(1) 1.578(2), Si(1)-O(2) 1.688(2), O(6)-Li(1) 2.015(5), Si(3)-O(3) 1.581(2), Si(3)-O(4) 1.684(3), Si(5)-O(5) 1.578(2), Si(5)-O(6) 1.688(3), Li(1)-O(1)-Li(2)' 84.5(2), Li(1)-O(1)-Li(3)' 113.2(2), Li(3)-O(3)-Li(1) 84.2(2), Li(1)-O(3)-Li(2)' 79.3(2), Li(2)-O(5)-Li(3) 84.5(2), Li(2)-O(5)-Li(1) 112.9(2), Li(3)-O(5)-Li(1) 78.8(2). Symmetry operation: ' –x, -y+1, -z.



Comment

The title complex, $[LiOSi(Me)_2OC(H)_2SiMe_3]_6$ **I**, crystallized from a solution of $LiCH_2SiMe_3$ (1M in hexane/diethyl ether) which had been stored at –30°C in a Schlenk flask, the stopper of which was sealed by silicone grease, over 3 weeks. Presumably, the compound is formed *via* the insertion of $OSiMe_2O$ fragments of the silicone grease into the Li-C bond of the lithium alkyl. Similar reactions of lithium alkyls, lithium phosphides etc. with silicone grease have been reported and the area has recently been reviewed.[1] The molecular structure of the compound (Figure 1) shows it to exist as a hexamer with a hexagonal prismatic Li_6O_6 core. Several related hexameric lithium silanolates have been previously reported, e.g. $[LiOSiMe_2Bu^t]_6$ [2] which contains three-coordinate Li centers. The lithium centers of **I** are, however, four-coordinate due to secondary coordination from the silanolate arms of the compound which give rise to four-membered LiO_2Si rings. All the bond lengths and angle of the structure are in the normal ranges. [3]

Experimental

$[LiOSi(Me)_2OC(H)_2SiMe_3]_6$ I:

Storing a solution of $LiCH_2SiMe_3$ (1M in hexane/diethyl ether) in a Schlenk flask, the stopper of which was sealed by silicone grease, at –30°C over 3 weeks led to the deposition of *ca.* 50 mg of **I** as colorless crystals. M.p. 185 – 187°C. IR/Nujol 1246 m, 1120 m, 1044 m, 857 m, 692 m. No NMR data could be obtained on this compound due to its low solubility in all standard deuterated solvents.

Crystallography:

Table 1. $[LiOSi(Me)_2OC(H)_2SiMe_3]_6.(hexane)_{0.5}$

Formula	$C_{39}H_{109}Li_6O_{12}Si_{12}$	Formula weight	1148.98
Crystal system	triclinic	Crystal size, mm	0.25x0.20x0.15
Space Group	*P*-1	*a*, Å	12.597(3)
b, Å	13.163(3)	*c*, Å	14.356(3)
α^o	112.03(3)	β^o	100.09(3)
γ^o	112.34(3)	*V*, Å^3	1895.9(7)
Z	1	Diffractometer	Nonius Kappa CCD
Temperature, K	150(2)	μ(Mo-K$_\alpha$), mm^{-1}	0.245
D_{calcd}, g cm^{-3}	1.006	*F*(000)	625
θ_{max}, ^{o}	27.49	Reflns meas.	16371
Reflns unique	8672	$R(F^2)$, $R_w(F^2)$ ($I>2\sigma(I)$)	0.0767, 0.2217
ρ, e Å^{-3}	2.353 (near Si1)	G.O.F.	1.098
No. obs/No. para	8672/313	Programs used	SHELX-97 [4]
Deposition number	CCDC 296417		

Acknowledgements

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References

[1] I. Haiduc, *Organometallics*, **23**, 3, (2004).
[2] F. Diedrich, U. Klingebiel, F. Dall'Antonia, C. Lehmann, M. Noltemeyer and T.R. Schneider, *Organometallics*, **19**, 5376 (2000).
[3] as determined from a survey of the Cambridge Crystallographic Database, January, 2006.
[4] G.M. Sheldrick, *SHELX-97*, University of Göttingen, Germany (1997).