# The First *X*-Ray Crystal Structural Characterizations of Alkali Metal Alkyl Thiolates: *X*-Ray Crystal Structures of $[Li_2(thf)_4\{SCH(SiMe_3)_2\}_2]$ and $[Li_2(thf)_{3.5}\{SC(SiMe_3)_3\}_2]$ (thf = tetrahydrofuran)

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The isolation and *X*-ray structural characterization of $[Li_2(thf)_4\{SCH(SiMe_3)_2\}_2]$ (**1**) and $[Li_2(thf)_{3.5}\{SC(SiMe_3)_3\}_2]$ (**2**) (thf = tetrahydrofuran) show them to be dimers with a central $Li_2S_2$ core (Li–S distances average 2.43 Å); the lithium atoms have approximately tetrahedral co-ordination and each sulphur is three-co-ordinate, being pyramidal in (**1**) and almost planar in (**2**) where severe crowding is evident.

There is considerable current interest in the structures and physical properties of organolithium compounds.[1,2] These studies are being gradually extended to include lithium derivatives of other species such as amides[3,4] and alkoxides.[5,6] In the heavier main group elements, although the structures of two lithium silyl derivatives have been known for some years[7] the first *X*-ray crystal structures of lithium diorganophosphides[8—10] and arsenides[10,11] were only recently reported. We now report the extension of the range of lithium complexes to the group 6B elements and give details of the first *X*-ray crystal structures of lithium alkyl thiolates.[12] These complexes, $[Li_2(thf)_4\{SCH(SiMe_3)_2\}_2]$ (**1**) and $[Li_2(thf)_{3.5}\{SC(SiMe_3)_3\}_2]$ (**2**), (thf = tetrahydrofuran) were synthesized by treatment of the thiols[13] with one equivalent of $Bu^nLi$ in hexane in the presence of small amounts of thf. Reduction in volume of the solution and cooling to −20 °C resulted in colourless crystals of (**1**) or (**2**) in almost quantitative yield.

$$[Li_2(thf)_4\{SCH(SiMe_3)_2\}_2]$$
(**1**)

$$[Li_2(thf)_{3.5}\{SC(SiMe_3)_3\}_2]$$
(**2**)

The structures of (**1**) and (**2**) are illustrated in Figures 1 and 2. *Crystal data:* (**1**), $C_{30}H_{70}Li_2O_4S_2Si_4$, $M = 685.24$, monoclinic, space group $P2_1/c$, $a = 11.380(2)$, $b = 21.905(4)$, $c = 9.059(2)$ Å, $\beta = 112.17(1)°$, $U = 2091(1)$ Å$^3$, $D_c = 1.09$ g cm$^{-3}$ for $Z = 2$, $\lambda(Cu\text{-}K_\alpha) = 1.54178$ Å, $\mu = 24.7$ cm$^{-1}$, 3302 reflections with $I > 2\sigma(I)$, $R = 0.072$. (**2**), $C_{34}H_{82}Li_2O_{3.5}Si_6S_2$, $M = 793.56$, monoclinic, space group $C2/c$, $a = 18.581(4)$, $b = 15.612(9)$, $c = 33.574(6)$ Å, $\beta = 93.04(2)°$, $U = 9726(4)$ Å$^3$, $D_c = 1.08$ g cm$^{-3}$ for $Z = 8$, $\lambda(Cu\text{-}K_\alpha) = 1.54178$ Å, $\mu = 26.7$ cm$^{-1}$, 5650 reflections with $I > 2\sigma(I)$, $R = 0.073$.†

Both complexes are dimers [(**1**) is centrosymmetric] having a core comprised of a rhombus of two lithium and two sulphur atoms. Each sulphur atom is three-co-ordinate being bonded to two lithiums and a carbon atom. The geometry at sulphur in (**1**) is pyramidal, the sum of the angles at sulphur being 321.4°. In sharp contrast the sulphur atoms in (**2**) are almost planar. This is probably a result of the more severe steric congestion in (**2**). A similar tendency towards planarity has been noted in the case of bulky lithium alkoxides which are more crowded because Li–O[14] distances are *ca.* 0.4 Å shorter than their Li–S analogues. The lithium–sulphur distances in (**1**) and (**2**) are similar averaging 2.41 Å. These values are close to those seen in the *X*-ray powder diffraction study of LiSMe[15] (2.4 Å) and the unreported *X*-ray crystal structure of the monomeric $[Li(thf)_3SC_6H_2Bu^t_3\text{-}2,4,6]$.[16] The carbon–sulphur bond lengths in (**2**) (1.890 Å average) are also longer than the corresponding distances in (**1**) (1.862 Å). This phenomenon, in conjunction with the long C(S)–Si distances (average 1.891 Å) attests to the larger steric requirements of the $-C(SiMe_3)_3$ *vs.* the $-CH(SiMe_3)_2$ group [average C(S)–Si distances 1.869 Å]. Bond lengths and angles of the remainder of the organosilyl groups are similar to those seen on other $CH(SiMe_3)_2$[10,17] and $C(SiMe_3)_3$[17] derivatives.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

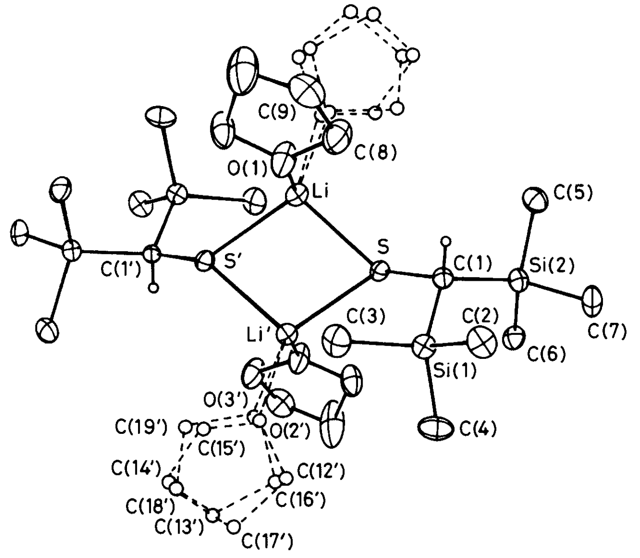

**Figure 1.** Bond distances (Å) and angles (°) for (**1**): Li–S 2.439(10), Li'–S 2.450(7), S–C(1) 1.862(4), Li · · · Li' 3.102(17), Li–O(1) 1.957(10), Li–O(2) 2.116(9), Li–O(3) 1.935(10), Si(1)–C(1), C(2), C(3), C(4) 1.866(4), 1.874(4), 1.859(6), 1.872(5), similar distances are found for bonds to Si(2); Li–S–Li' 78.8(3), S–Li–S' 101.3(3), S–Li–O(1) 120.2(3), S–Li–O(2) 104.1(4), S–Li–O(3) 106.8(5), C(1)–S–Li 113.2(2), C(1)–S–Li' 129.4(2), S–C(1)–Si(1) 111.2(2), S–C(1)–Si(2) 106.5(2), C(1)–Si(1)–C(2) 110.6(2), C(1)–Si(1)–C(3) 111.8(2), C(1)–Si(1)–C(4) 110.5(2), C(2)–Si(1)–C(3) 105.2(2), C(2)–Si(1)–C(4) 108.5(2), C(3)–Si(1)–C(4) 110.1(2), angles at Si(2) are similar. Primed atoms are at symmetry position $1 - z, -y, 2 - z$.

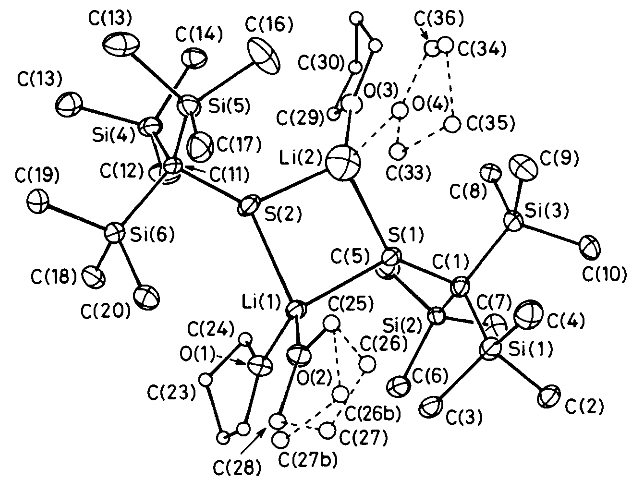

**Figure 2.** Bond distances (Å) and angles (°) for (**2**): S(1)–Li(1) 2.494(9), S(1)–Li(2) 2.328(19), S(2)–Li(1) 2.485(9), S(2)–Li(2) 2.354(19), Li(1) · · · Li(2) 3.437(16), S(1)–C(1) 1.894(5), S(2)–C(11) 1.885(5), C(1)–Si(1) 1.894(6), C(1)–Si(2) 1.892(6), C(1)–Si(3) 1.885(6), average Si–C in SiMe$_3$ groups 1.874(8), Li(1)–O(1) 1.961(10), Li(1)–O(2) 1.956(10), Li(2)–O(3) 1.918(19), Li(2)–O(4) 2.458(20), Li(1)–S(1)–Li(2) 90.9(5), Li(1)–S(2)–Li(2) 90.5(5), S(1)–Li(1)–S(2) 85.8(3), S(1)–Li(2)–S(2) 92.8(7), Li(1)–S(1)–C(1) 132.0(3), Li(2)–S(1)–C(1) 134.5(3), Li(1)–S(2)–C(11) 137.1(3), Li(2)–S(2)–C(11) 130.4(5), S(1)–C(1)–Si(1) 103.3(3), S(1)–C(1)–Si(2) 106.9(3), S(1)–C(1)–Si(3) 107.4(3), S(1)–C(1)–Si(2) 113.2(3), Si(1)–C(1)–Si(3) 113.0(3), Si(2)–C(1)–Si(3) 112.3(3), C(1)–Si(1)–C(2) 113.2(3), C(1)–Si(1)–C(2) 114.7(3), C(1)–Si(1)–C(4) 111.5(3), C(2)–Si(1)–C(3), 103.8(3), C(2)–Si(1)–C(4), 106.5(3), C(3)–Si(1)–C(4) 106.3(3).

In both (**1**) and (**2**) the lithium atoms are four-co-ordinate with approximately tetrahedral geometry. The Li–O bond distances are typical except in the case of the shared thf molecule in (**2**).[1,2] In (**1**) a thf molecule is disordered but a smooth refinement ensued when the thf molecule was allowed to occupy two approximately equivalent sites. In (**2**) one thf molecule has a similar disorder. A second thf molecule, that of O(4), is disordered around a $C_2$ axis, and a good refinement was obtained by assuming 50% occupancy by the thf on neighbouring molecules of (**2**). This thf is loosely bound, as shown by the long Li–O distance of 2.46(2) Å.

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