

**(μ -Tri-*tert*-butoxysilanethiolato)bis-
[(tetrahydrofuran)lithium(I)] and
catena-poly[[bis(μ -tri-*tert*-butoxy-
silanethiolato)dilithium(I)]- μ -di-
methoxyethane]: solvent coordina-
tion as the structure-forming factor**

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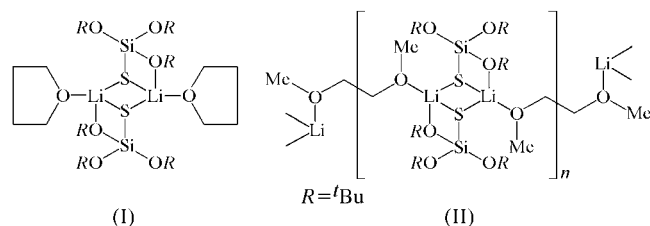
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The title compounds, μ -(tri-*tert*-butoxysilanethiolato- $\kappa^2S:S$)-bis[(tetrahydrofuran- κO)lithium(I)], $[\text{Li}_2(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_2(\text{C}_4\text{H}_8\text{O})_2]$, (I), and catena-poly[[bis(μ -tri-*tert*-butoxysilanethiolato)-1:2 κ^2S :1 κS :2 $\kappa S,O$ -dilithium(I)]- μ -dimethoxyethane- $\kappa^2O:O'$], $[\text{Li}_2(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_2(\text{C}_4\text{H}_{10}\text{O}_2)]_n$, (II), were obtained by the reaction of tri-*tert*-butoxysilanethiol with metallic lithium. The crude product, when recrystallized from tetrahydrofuran (THF) yields (I), and when recrystallized from 1,2-dimethoxyethane (DME) gives (II). Compound (I) forms centrosymmetric dimers in the solid state with an Li_2S_2 central core, whereas (II) forms infinitely long chains, in which the centrosymmetric dimeric units are linked together by the bidentate DME ligand (also residing on an inversion centre), thus forming a coordination polymer. The formation of a one-dimensional structure in (II) is a consequence of replacement of a monodentate THF solvent molecule with a bidentate DME molecule.

Comment

Structural studies on thiolates, selenolates and tellurolates of the *s*-block elements are important because the compounds often serve as starting materials in both inorganic and organic syntheses (Englich & Ruhlandt-Senge, 2000). The most common structural features observed for the lithium derivatives are monomeric or dimeric formulations, but lithium chalcogenolate chemistry has seen higher degrees of aggregation, *e.g.* trimers, tetramers or hexamers. A metal coordination number of four is observed for the majority of these compounds (Niemeyer & Power, 1996; Ruhlandt-Senge *et al.*, 1996; Ellison & Power, 1994; Janssen *et al.*, 1996). The structure and chemistry of silanethiolates have been the subject of research by us (Wojnowski *et al.*, 1985, 1994) and other groups

(Kovacs *et al.*, 2000; Komuro *et al.*, 2002, 2003). We have attempted to introduce a different type of thiolate ligand, which contains S bound to an Si atom instead of a C atom. A tri-*tert*-butoxysilanethiolate ligand, $(\text{tBuO})_3\text{SiS}^-$, has been used in much of our work because of its unique features, namely the large steric hindrance at the Si atom created by the three bulky *tert*-butoxy groups, its chelating capability as an O- and S-donor ligand, and its non-polar exterior and polar interior.



Most of the papers mentioned above concern the silanethiolates of transition metals (Becker *et al.*, 1992) and of the *p*-block metals (Wojnowski, Wojnowska *et al.*, 1986; Peters *et al.*, 1997). However, structural data regarding silanethiolates of alkali metals are scarce (Wojnowski, Peters *et al.*, 1986; Chadwick *et al.*, 1997) and only one report describes a lithium silanethiolate (Baranowska *et al.*, 2002). We present here the structures of two new lithium silanethiolates, namely the title compounds (I) and (II).

Compound (I), $[(\text{tBuO})_3\text{SiSLi}(\text{THF})]_2$ (THF is tetrahydrofuran), resides on an inversion centre and comprises two silanethiolate ligands (Fig. 1). Each S atom bridges two Li^+ cations, forming a planar central Li_2S_2 core, with two THF

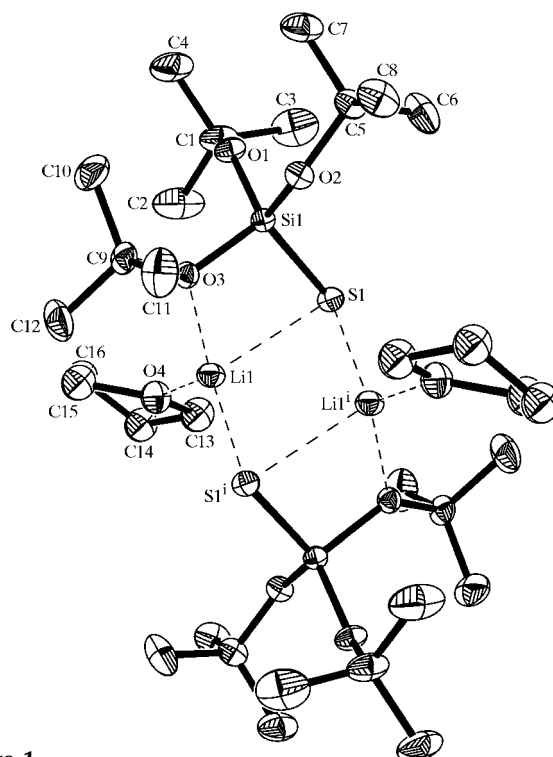


Figure 1
The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted. [Symmetry code: (i) $1 - x, -y, -z$.]

molecules bound to the two Li atoms. The THF molecules are disordered [site-occupancy factors 0.693 (16)/0.307 (16)] and are positioned above and below the Li_2S_2 plane. Additionally, atom O3 from each of the two silanethiolate ligands chelates the Li atom, resulting in an distorted tetrahedral S,S,O,O -coordination of the Li cores, with ‘tetrahedral’ angles between 79.9 (2) and 120.2 (3)°. The longer Si—O3 bond is a consequence of chelation of the Li atom by O3. The Si—S bond length in (I) is considerably shorter than the distance in covalent silanethiolate compounds and is comparable with the values observed in ionic silanethiolate compounds (Becker *et al.*, 2004).

Compound (II) (Fig. 2), $[\{(\text{BuO})_3\text{SiSLi}\}_2(\text{DME})]_n$ (DME is 1,2-dimethoxyethane), resides on an inversion centre and exhibits an apparently similar dimeric structure to (I). The dimer halves are related to each other by an inversion centre located at the centre of the Li_2S_2 unit, a planar four-membered ring of alternating Li and S atoms. Again, each Li cation is surrounded, in a distorted tetrahedral fashion, by two S and two O atoms. One of the three butoxy groups of the thiolate ligand supplies the first chelating O atom and the second O atom comes from the DME molecule. The Si—O bond is considerably longer for the bond to the chelating O3 atom. The ‘tetrahedral’ angles at the Li atom range from 80.61 (15) to 122.6 (2)°. The smallest angle is observed between the chelating donors, *i.e.* O3—Li1—S1, while the largest angle, O3—Li1—O4, can be found between the heteroleptic donor atoms. Molecules of (I) and (II) are examples of lithium thiolates with short Li··Li contacts of 2.889 (14) and 2.788 (9) Å, respectively. Similar distances can be found in $\text{LiOH}\cdot\text{H}_2\text{O}$ (Ojamäe *et al.*, 1994).

The title compounds consist of very similar dimeric units, but there is a basic difference between them. Compound (I) has Li^+ cations coordinated by a THF molecule and having

only one donor atom, generating an isolated dimer, whereas compound (II) has Li^+ cations coordinated by a DME molecule containing two O-donor atoms: the first (O4) coordinates to atom Li1, while the second (O4ⁱⁱ) coordinates to atom Li1ⁱⁱ from the neighbouring dimeric unit (Fig. 2; symmetry code as in Fig. 2). This arrangement combines the dimers together into infinitely long chains, in contrast to (I). The chain of the coordination polymer passes parallel to the *b* axis.

Dimers of (I) and chains of (II) are free of intermolecular interactions, apart from van der Waals forces. Compound (II) is thus an example of a coordination polymer (Braga *et al.*, 2005) in which monomeric units are linked by coordination bonds. This study shows the fundamental role a solvent can play in the formation of the overall structure of solvated salts. The formation of a higher-order structure, namely the polymeric chains, was made possible by the replacement of a monodentate solvent by a bidentate one.

Experimental

The synthesis was carried out using a standard vacuum, an N_2 line and Schlenk techniques. Both compounds were synthesized by direct reaction of $(\text{BuO})_3\text{SiSH}$ (Piękoś & Wojnowski, 1962) with an excess of metallic lithium. The mixture was stirred and heated for 4 h, yielding a white precipitate. To dissolve this, tetrahydrofuran (THF) was added to part of the precipitate. The solution was separated from the excess metal by filtration, and crystallization by slow evaporation of the solvent afforded colourless crystals of (I) suitable for X-ray diffraction analysis. The second part of the white precipitate was dissolved in 1,2-dimethoxyethane (DME) and filtered in order to separate excess lithium. Colourless crystals of (II) were obtained by crystallization from DME. Crystals of (I) and (II) are stable at room temperature and are fairly resistant to oxidation but sensitive to moist air, which makes diffraction experiments possible only at low temperatures, preferably 200 K and below.

Compound (I)

Crystal data

$[\text{Li}_2(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_2(\text{C}_4\text{H}_8\text{O})_2]$
 $M_r = 717.06$
 Monoclinic, $P2_1/n$
 $a = 9.789$ (2) Å
 $b = 20.083$ (4) Å
 $c = 11.746$ (2) Å
 $\beta = 111.52$ (3)°
 $V = 2148.2$ (8) Å³
 $Z = 2$

$D_x = 1.109$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 47 reflections
 $\theta = 2.3$ – 17.5 °
 $\mu = 0.22$ mm⁻¹
 $T = 200$ (2) K
 Block, colourless
 $0.5 \times 0.4 \times 0.2$ mm

Data collection

Kuma KM-4 diffractometer with point detector
 $\omega/2\theta$ scans
 4228 measured reflections
 4007 independent reflections
 2806 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.071$

$\theta_{\text{max}} = 25.6$ °
 $h = -11 \rightarrow 11$
 $k = 0 \rightarrow 24$
 $l = -13 \rightarrow 0$
 3 standard reflections
 every 200 reflections
 intensity decay: 8.4%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.220$
 $S = 1.13$
 4007 reflections
 212 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1129P)^2 + 2.9823P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.50$ e Å⁻³

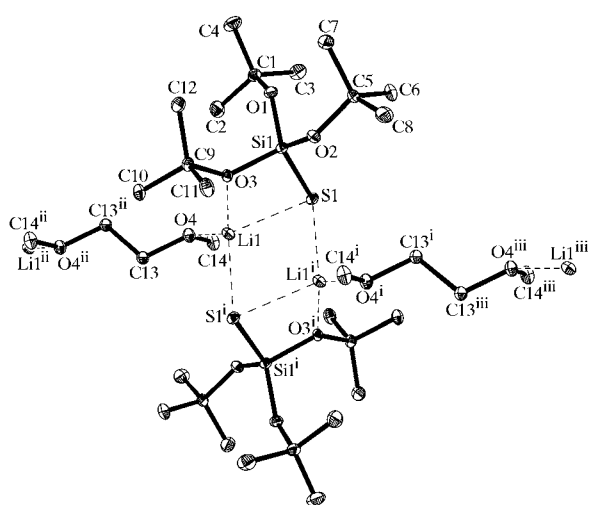


Figure 2

The molecular structure of (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted. The asymmetric unit contains a $(\text{BuO})_3\text{SiS}^-$ anion, an Li^+ cation and half the DME molecule. To illustrate the polymeric nature of (II), two DME molecules are shown, together with related cations Li1ⁱⁱ (left) and Li1ⁱⁱⁱ (right). [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, 1 - z$; (iii) $-x, -1 - y, -z$.]

Table 1
Selected geometric parameters (Å, °) for (I).

Si1—Si1	2.0515 (16)	Si1—O2	1.626 (3)
Si1—Li1 ⁱ	2.429 (7)	Si1—O3	1.666 (3)
Si1—Li1	2.521 (7)	Li1—O3	1.992 (7)
Si1—O1	1.625 (3)	Li1—O4	1.929 (8)
Si1—Si1—Li1 ⁱ	106.91 (17)	O4—Li1—Si1 ⁱ	120.2 (3)
Si1—Si1—Li1	75.48 (16)	O4—Li1—S1	110.7 (3)
Li1 ⁱ —Si1—Li1	71.4 (3)	O3—Li1—O4	118.9 (4)
O3—Li1—S1	79.9 (2)	Si1 ⁱ —Li1—S1	108.6 (3)
O3—Li1—Si1 ⁱ	110.9 (3)	O4—Li1—Li1 ⁱ	137.0 (5)

Symmetry code: (i) 1 - x, -y, -z.

Compound (II)

Crystal data

[Li ₂ (C ₁₂ H ₂₇ O ₃ SSi) ₂ (C ₄ H ₁₀ O ₂) ₂]	Z = 2
<i>M_r</i> = 331.49	<i>D_x</i> = 1.124 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 8.721 (2) Å	Cell parameters from 3123 reflections
<i>b</i> = 9.305 (2) Å	<i>θ</i> = 2–20°
<i>c</i> = 14.048 (3) Å	<i>μ</i> = 0.24 mm ⁻¹
<i>α</i> = 82.24 (3)°	<i>T</i> = 120 (2) K
<i>β</i> = 72.91 (3)°	Rod, colourless
<i>γ</i> = 64.01 (3)°	0.4 × 0.2 × 0.2 mm
<i>V</i> = 979.4 (5) Å ³	

Data collection

Kuma KM-4 diffractometer with Sapphire2 CCD area detector	<i>R</i> _{int} = 0.027
<i>ω</i> scans, 612 frames	<i>θ</i> _{max} = 25.5°
5576 measured reflections	<i>h</i> = -8 → 10
3638 independent reflections	<i>k</i> = -11 → 11
3362 reflections with <i>I</i> > 2σ(<i>I</i>)	<i>l</i> = -16 → 16

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 2.4894P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	(<i>Δ</i> / <i>σ</i>) _{max} = 0.001
<i>S</i> = 1.05	<i>Δρ</i> _{max} = 0.54 e Å ⁻³
3638 reflections	<i>Δρ</i> _{min} = -0.45 e Å ⁻³
191 parameters	
H-atom parameters constrained	

Table 2
Selected geometric parameters (Å, °) for (II).

Si1—Si1	2.0629 (13)	Si1—O2	1.633 (2)
Si1—Li1 ⁱ	2.444 (4)	Si1—O3	1.6587 (18)
Si1—Li1	2.509 (4)	Li1—O3	1.962 (5)
Si1—O1	1.6290 (19)	Li1—O4	1.946 (5)
Si1—Si1—Li1 ⁱ	108.86 (11)	O4—Li1—S1	112.28 (19)
Si1—Si1—Li1	74.89 (11)	O3—Li1—S1	80.61 (15)
Li1 ⁱ —Si1—Li1	68.50 (17)	Si1 ⁱ —Li1—S1	111.50 (17)
O4—Li1—O3	122.6 (2)	Si1 ⁱ —Li1—Li1 ⁱ	56.86 (15)
O4—Li1—Si1 ⁱ	110.81 (19)	S1—Li1—Li1 ⁱ	54.64 (14)
O3—Li1—Si1 ⁱ	115.2 (2)		

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

All H atoms were refined as riding, with C—H distances in the range 0.97–0.99 Å and with *U*_{iso}(H) = 1.2*U*_{iso}(C). The disorder of the THF molecule in (I) was determined by constraining the ellipsoids

of atoms C14–C16 to be the same [EADP instruction in *SHELXL97* (Sheldrick, 1997)]. Additionally, the C13–C14 and O4–C16 bonds were constrained to be equal in both disordered parts (SADI in *SHELXL97*). Note that data for (I) were measured at 200 K and for (II) at 120 K.

Data collection: *KM-4 Software* (Galdecki *et al.*, 1996) for (I); *CrysAlis CCD* (Oxford Diffraction, 2003) for (II). Cell refinement: *KM-4 Software* for (I); *CrysAlis RED* (Oxford Diffraction, 2003) for (II). Data reduction: *DATAPROC* (Galdecki *et al.*, 1996) for (I); *CrysAlis RED* for (II). For both compounds, structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); publication software: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1262). Services for accessing these data are described at the back of the journal.

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