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The first compound with an unusual type of anion, $[Li(SR)_2]^-$: bis(μ_2-aqua-d_2)tetrakis(aqua-d_2)-dilithium(I) bis[bis(tri-*tert*-butoxysilanethiolato-κ^2O,S)lithate(I)] dihydrate-d_2

Magdalena Kloskowska, Jarosław Chojnacki, Wiesław Wojnowski and Barbara Becker*

Department of Inorganic Chemistry, Chemical Faculty, Gdańsk University of Technology, 11/12 G. Narutowicz Street, 80952 PL Gdańsk, Poland
Correspondence e-mail: bbecker@chem.pg.gda.pl

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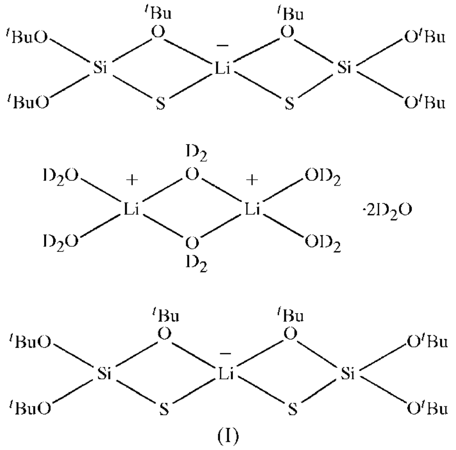
The title complex, $[Li_2(D_2O)_6][Li(C_9H_{27}SSiO_3)_2]_2\cdot 2D_2O$, is the first compound with an S—*M* bond (*M* = alkali metal) within an unusual type of lithate anion, $[Li(SR)_2]^-$ {where *R* is $Si[OC(CH_3)_3]_3$}. There is a centre of symmetry located in the middle of the Li_2O_2 ring of the cation. All Li atoms are four-coordinate, with LiO_4 (cations) and LiO_2S_2 (anions) cores. The singly charged $[Li(SR)_2]^-$ anions are well separated from the doubly charged $[Li_2(D_2O)_6]^{2+}$ cations; the distance between Li atoms from differently charged ions is greater than 5 Å. Both ion types are held within an extended network of O—D···O and O—D···S hydrogen bonds.

Comment

Thiolates, selenolates and tellurolates of the *s*-block elements are very often used as precursors of chalcogenolates of other metals. Special attention has therefore been devoted to their structure, which can sometimes be controlled by an appropriate method of synthesis (Englich & Ruhlandt-Senge, 2000). The most common lithium thiolates are monomeric (Chadwick & Ruhlandt-Senge, 1998; Ives *et al.*, 2003) or dimeric (Bjernemose *et al.*, 2004; Komuro *et al.*, 2004). However, trimeric (Ruhlandt-Senge *et al.*, 1996; Niemeyer & Power, 1996), hexameric (Janssen *et al.*, 1996) and polymeric forms (Ruth *et al.*, 2005; Hampe *et al.*, 2005) are also known. In the case of lithium compounds, where the most common coordination number is four, the central atoms are frequently coordinated by solvent molecules, with O– and N-donor solvents preferred.

Silanethiolates of the *s*-block metals are much less numerous and the structural data of only a few alkali metal derivatives have been described to date. Compounds with Si—S—Li (Baranowska *et al.*, 2002; Komuro *et al.*, 2004; Jesionka *et al.*, 2005) and Si—S—Na bond systems (Wojnowski *et al.*, 1986; Chadwick *et al.*, 1997) have been reported. None of them, however, is similar to the title compound, (I), described in the present paper. This lithate is not only the first compound with an S—Li bond within the $[M(SR)_2]^-$ type of anion {where *M* is an alkali metal and *R* is $Si[OC(CH_3)_3]_3$}, but is also the first ionic thiolate where both ions are metal complexes and both are based on lithium.



(I)

Compound (I) can be obtained using the procedure described in the *Experimental* section. Fig. 1 shows the complete parts of complex (I), along with the atom-numbering scheme. Selected bond lengths and angles are presented in Table 1. Because of the doubly charged complex bimetallic lithium cation, two singly charged complex lithate anions are required to balance the charge. Two heavy-water solvent molecules complete the structure.

The central atom in the lithate $[Li(SR)_2]^-$ anion is coordinated by two silanethiolate S atoms and two siloxy O atoms from two undoubtedly chelating $(^tBuO)_3SiS^-$ ligands. This leads to the central LiO_2S_2 core which, due to the O—Li—S

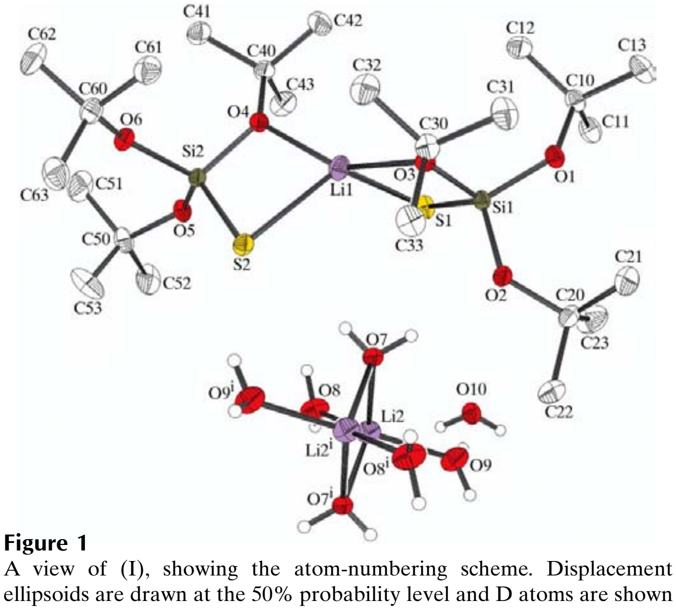


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and D atoms are shown as small spheres of arbitrary radii. H atoms have been omitted for clarity. [Symmetry code: (i) $-x, -y + 1, -z + 1$.]

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chelate bite angle, shows a severely distorted tetrahedral arrangement of atoms, with angles between 80.29 (12) and 148.2 (2)°. The Li—S and Li—O bond lengths within the lithate anion seem to be unexceptional, being comparable with those found in two other known neutral lithium tri-*tert*-butoxysilanethiolates (Jesionka *et al.*, 2005). Moreover, the Li—O bond lengths in the lithate anion fall within the limits set by the bonds present in the accompanying $[Li_2(D_2O)_6]^{2+}$ cation. The cation contains two Li atoms, both coordinated only by O atoms from D_2O molecules. Two of these D_2O ligands are in bridging and four in terminal positions. The geometry of the resulting LiO_4 core can also be described as a distorted tetrahedron. Moreover, the bimetallic cation system created by the bridging molecules of heavy water leads to the formation of a planar centrosymetric $Li_2(\mu\text{-}O)_2$ ring.

Outside the bimetallic complex cation, two other heavy-water solvent molecules are present within the crystal structure. Their presence has important consequences. Although all heavy water molecules are engaged in the formation of hydrogen bonds, each ligating D_2O forms only two such bonds. On the other hand, each D_2O solvent molecule forms four hydrogen bonds. Each is simultaneously a donor of $O—D\cdots O$ and $O—D\cdots S$ hydrogen bonds to one of the $[Li(SR)_2]^-$ lithate anions and an acceptor of two $O\cdots D—O$ hydrogen bonds from two different $[Li_2(D_2O)_6]^{2+}$ cations. Both ion types are therefore held within an extended network of $O—D\cdots O$ and $O—D\cdots S$ hydrogen bonds. This is illustrated in Fig. 2 and data

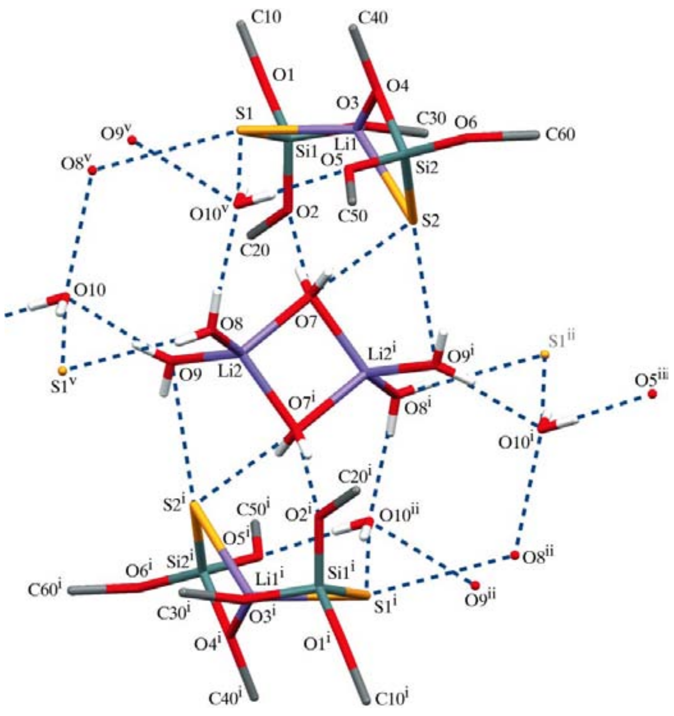

Figure 2
The hydrogen-bond network in (I). All methyl groups have been omitted for clarity. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x - 1, y, z$; (v) $-x + 1, -y + 1, -z + 1$.]

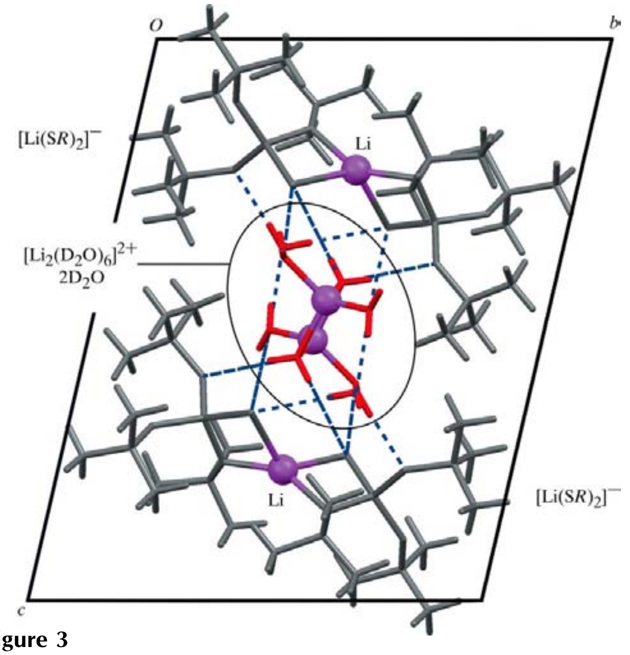

Figure 3
The arrangement of anions, cations and D_2O solvent molecules within the unit cell of (I), viewed along the *a* axis. Dashed lines represent hydrogen bonds.

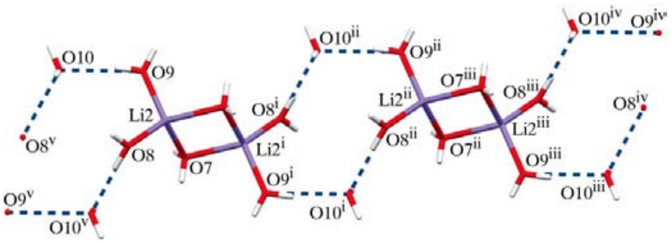

Figure 4
Interactions between the complex cations and D_2O solvent molecules, leading to the hydrogen-bond network running in the *a* direction. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x - 1, y, z$; (iii) $-x - 1, -y + 1, -z + 1$; (iv) $x - 2, y, z$; (v) $-x + 1, -y + 1, -z + 1$.]

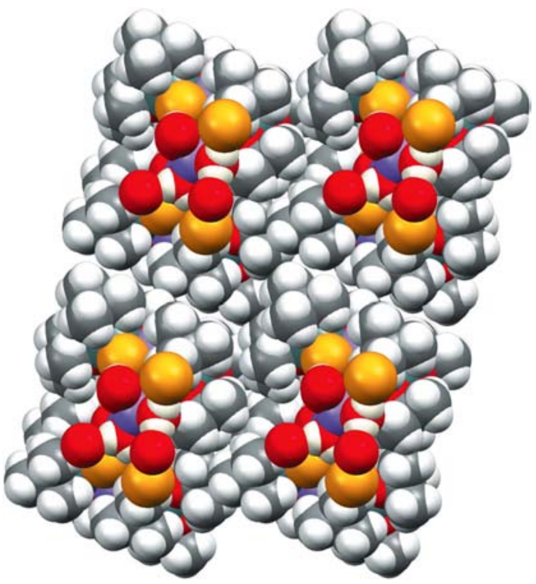

Figure 5
The packing of (I) in the crystal structure, viewed along the *a* axis.

for eight different hydrogen bonds are summarized in Table 2. The hydrogen-bond network in some respects 'covers' the bimetallic cations, which are located in the space between two lithate anions, as shown in Fig. 3. Because of these interactions between the complex cations and the D_2O solvent molecules, the one-dimensional hydrogen-bond network which is formed runs in the *a* direction, as shown in Fig. 4.

Isolation of the distinct ionic domains in compound (I) is further evidenced by the intermetallic distances. The bimetallic $[Li_2(D_2O)_6]^{2+}$ cation may serve as an example of a lithium complex, with an Li···Li distance of 2.876 (7) Å. A similar distance can be found in the $Li_2(\mu\text{-}S)_2$ ring in two neutral tri-*tert*-butoxysilanethiolates of lithium (Jesionka *et al.*, 2005). In the case of (I), the distances between the Li atom of the lithate anion and either of the two Li atoms within the cation are much larger, at 5.279 (5) and 5.261 (5) Å. In fact, the structure of (I) shown in Fig. 5 can be roughly described as side-by-side packed tetragonal columns interacting only by van der Waals forces. These columns, composed of negative lithate anions, have in their interior another columnar structure formed of complex cations, embedded with and covered by the hydrogen-bond network.

Experimental

The synthesis of (I) was carried out using standard vacuum-line (argon) and Schlenk techniques. All solvents were dried by standard methods and distilled under argon prior to use. An excess of freshly cut metallic lithium was added to a solution of $[(^tBuO)_3SiS]_3SnCl$ (3.12 mmol, 3.1 g) (Kloskowska *et al.*, 2006) in tetrahydrofuran (30 ml) and the mixture was stirred for 15 min at 313 K and then at room temperature for the next 3 d. The mixture was then filtered and heavy water (0.5 ml, 27.5 mmol) was added to the filtrate. Extraction with toluene and crystallization from *n*-hexane gave complex (I) (m.p. 431 K) in good yield, with consistent elemental analyses for C, H and S. EI MS (70 eV) *m*/*z*: 1186.5 ($\{[Li_2(D_2O)_2][Li(C_{12}H_{27}O_3SSi)_2]_2\}^+$, <15%).

Crystal data

$[Li_2(D_2O)_6][Li(C_{12}H_{27}O_3SSi)_2]_2\cdot 2D_2O$
$M_r = 1305.92$
Triclinic, $P\bar{1}$
$a = 8.5218$ (6) Å
$b = 14.0107$ (11) Å
$c = 17.4337$ (14) Å
$\alpha = 99.743$ (7)°
$\beta = 99.712$ (7)°
$\gamma = 105.197$ (7)°
$V = 1929.4$ (3) Å^3
$Z = 1$
$D_x = 1.124$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.24$ mm^{-1}
$T = 120$ (2) K
Prism, colourless
0.52 × 0.41 × 0.4 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
ω scans
13004 measured reflections
6815 independent reflections
6228 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\rm max} = 25.1°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.120$
$S = 1.06$
6815 reflections
411 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 2.0875P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.018$
$\Delta\rho_{\rm max} = 0.45$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Si1—O1	1.6270 (14)	Si2—S2	2.0519 (7)
Si1—O2	1.6456 (14)	S2—Li1	2.481 (4)
Si1—O3	1.6650 (14)	O4—Li1	1.983 (4)
Si1—S1	2.0549 (8)	O7—Li2	2.027 (4)
S1—Li1	2.493 (4)	O7—Li2^{i}	2.032 (4)
O3—Li1	1.972 (4)	O8—Li2	1.899 (4)
Si2—O6	1.6264 (14)	O9—Li2	1.901 (4)
Si2—O5	1.6463 (15)	Li2—Li2^{i}	2.876 (7)
Si2—O4	1.6663 (14)		
Si1—S1—Li1	75.55 (8)	S2—Li1—S1	123.98 (15)
Si2—S2—Li1	75.79 (8)	O8—Li2—O9	110.8 (2)
O3—Li1—O4	148.2 (2)	O8—Li2—O7	114.11 (19)
O3—Li1—S2	114.47 (16)	O9—Li2—O7	112.3 (2)
O4—Li1—S2	80.41 (13)	O8—Li2—O7^{i}	124.2 (2)
O3—Li1—S1	80.29 (12)	O9—Li2—O7^{i}	103.98 (18)
O4—Li1—S1	115.77 (16)	O7—Li2—O7^{i}	89.78 (16)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—D7*B*···S2	0.76 (3)	2.54 (3)	3.2765 (17)	163 (3)
O7—D7*A*···O2	0.83 (4)	2.08 (4)	2.906 (2)	170 (3)
O8—D8*B*···S1^{ii}	0.80 (4)	2.54 (4)	3.3192 (19)	164 (3)
O8—D8*A*···O10^{ii}	0.83 (4)	1.95 (4)	2.776 (2)	171 (4)
O9—D9*A*···O10	0.85 (3)	1.92 (3)	2.759 (2)	170 (3)
O9—D9*B*···S2^{i}	0.78 (3)	2.55 (3)	3.2584 (19)	151 (3)
O10—D10*A*···S1^{ii}	0.84 (4)	2.39 (4)	3.2086 (18)	168 (3)
O10—D10*B*···O5^{ii}	0.81 (4)	2.03 (4)	2.845 (2)	175 (3)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$.

Methyl H atoms were positioned geometrically and refined as riding on their parent C atoms, with C—H = 0.98 Å and $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$. Deuterium atoms from the heavy water molecules were found in a Fourier electron-density map and refined with no restraints. The highest electron-density peak in the final difference map is located 1.03 Å from atom Si1.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3045). Services for accessing these data are described at the back of the journal.

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