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Key indicators

Single-crystal X-ray study
 T = 150 K
 Mean $\sigma(C-C)$ = 0.004 Å
 R factor = 0.037
 wR factor = 0.145
 Data-to-parameter ratio = 18.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

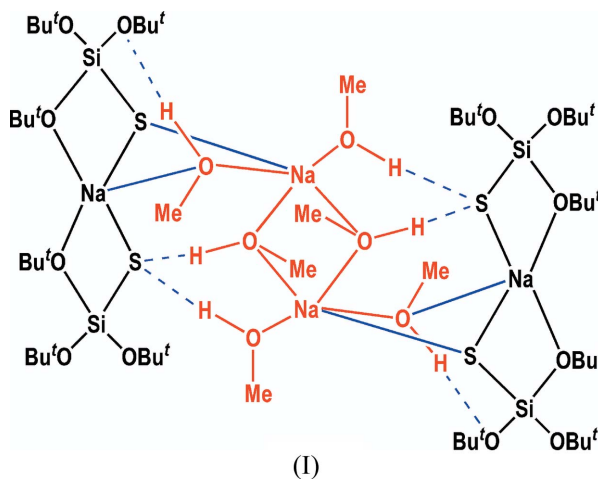
Tetrakis(μ_2 -methanol- $\kappa^2O:O$)bis(methanol- κO)-(μ_2 -tri-*tert*-butoxysilanethiolato- $\kappa^3S:O,S$)-bis(tri-*tert*-butoxysilanethiolato- κ^2O,S)-tetrasodium(I)

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The title compound, $[Na_4(C_{12}H_{27}O_3SSi)_4(CH_4O)_6]$, may be regarded as an assembly of short-contact ion triplets built of a dinuclear $[Na_2(MeOH)_6]^{2+}$ cation and two $[Na\{SSi(O^tBu)_3\}_2]^-$ anions, related by a centre of symmetry. The presence of sulfur and oxygen bridges, as well as $O-H \cdots O$ and $O-H \cdots S$ hydrogen bonds, results in a tetranuclear complex with all Na atoms pentacoordinated. The complex sits on a centre of symmetry.

Comment

The preparative importance of alkali metal thiolates and their structural properties still generate interest in this group of compounds. Sodium thiolates, which can form structures from monomeric (Englich & Ruhlandt-Senge, 2000; Chadwick & Ruhlandt-Senge, 1998) to polymeric (Englich & Ruhlandt-Senge, 2000; Hernandez-Arganis *et al.*, 2004), are one example of this class of compounds. Only three sodium silanethiolates have been reported to date, namely the trihydrate (Wojnowski *et al.*, 1986) and toluene solvate (Chadwick *et al.*, 1997) of sodium triphenylsilanethiolate, and the tetrahydrofuran solvate of sodium phenyl-di-*tert*-butylsilanethiolate (Kückmann *et al.*, 2005). They show substantial structural variability, from the non-molecular ionic structure of $Ph_3SiSNa \cdot 3H_2O$ to the cubane-like tetrameric molecule of $[Ph^tBu_2SiSNa \cdot THF]_4$. In this paper, we report a new type of sodium silanethiolate, the title compound, $[Na_2(MeOH)_6][Na\{SSi(O^tBu)_3\}_2]_2$, (I).



Compound (I) is centrosymmetric. Two $Na\{SSi(O^tBu)_3\}_2^-$ components (black in the scheme) are located in positions related by the centre of symmetry at the midpoint of the $[Na_2(CH_3OH)_6]^{2+}$ unit (red in the scheme). The two anionic

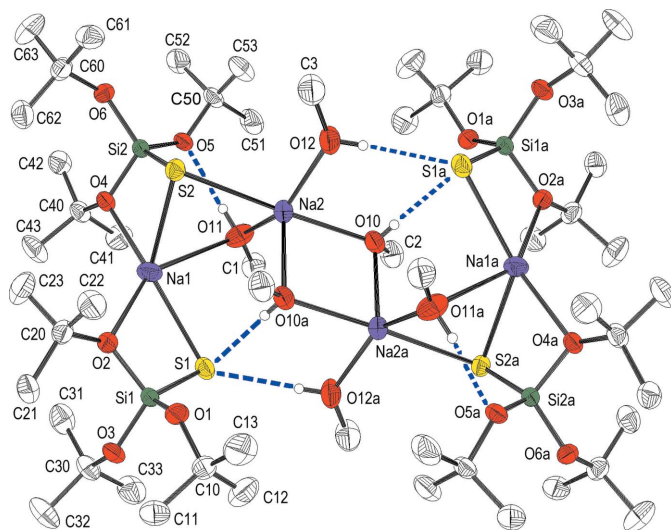


Figure 1

A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydroxyl H atoms are represented as circles of arbitrary size and methyl H atoms have been omitted for clarity. Dashed lines indicate hydrogen bonds. [Symmetry code (a): $1 - x, 2 - y, 1 - z$.]

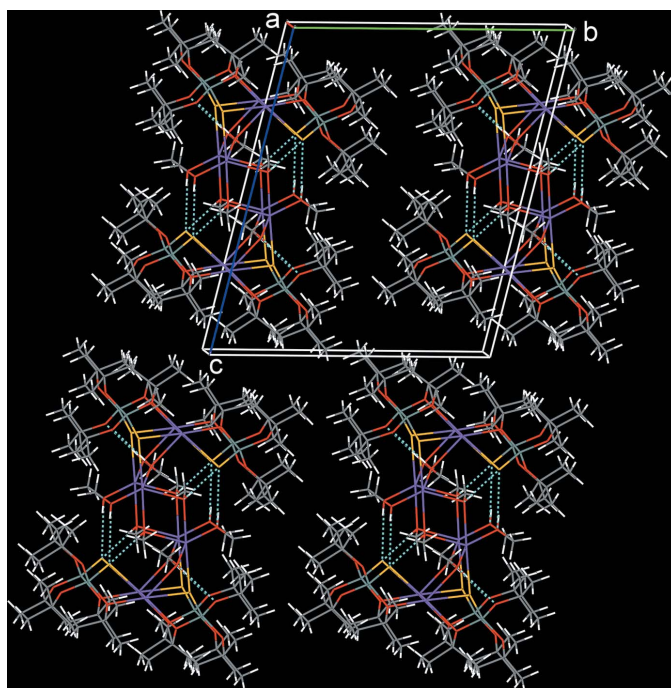


Figure 2

A packing diagram of (I), viewed along the *a* axis. Na atoms are violet, C atoms grey, S atoms yellow, Si atoms grey-green, O atoms red and H atoms white. Dashed lines indicate hydrogen bonds.

fragments are formed by the two exterior Na atoms, which are both coordinated by two (^tBuO)₃SiS groups, here operating in a chelating mode. S atoms form two bridges between the anions and the cation, and the three charged fragments are additionally linked by two bridging methanol molecules and six hydrogen bonds of the types O—H···S and O—H···O (blue in the scheme).

The molecular structure of (I) is shown in Fig. 1 and its crystal packing in Fig. 2. It has no close structural analogues. However, because it can be regarded as an assembly of three ions, its structure is somewhat similar to that of the recently obtained lithiate $\{[\text{Li}_2(\text{D}_2\text{O})_6][\text{Li}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2]_2 \cdot 2\text{D}_2\text{O}$ (Kloskowska, Chojnacki, Wojnowski & Becker, 2006). This is only a limited similarity, because the distinct ion separation observed in the lithiate is absent in (I). Therefore, although the description of (I) as a short-contact ion triplet is plausible, it seems more appropriate to designate it a tetranuclear complex.

The lengths of the Na—S and Na—O bonds in (I) do not differ significantly from those found in other sodium silanethiolates. The mean value of the Si—S bonds (2.050 Å) is shorter by *ca* 0.03 Å and comparable to that found in the above-mentioned lithiate.

Compound (I) is a rare example of a sodium thiolate with Na···Na short contacts of *ca* 3.6 Å. Similar distances have been found in only a few tetramers (Chadwick *et al.*, 1997) and hexamers (Kückmann *et al.*, 2005).

Experimental

The synthesis was carried out using standard vacuum–nitrogen line and Schlenk techniques. All solvents were dried by standard methods and distilled under argon prior to use. Compound (I) was synthesized by the addition of [^tBuO)₃SiS]₃SnBr (1 g, 0.964 mmol) (Kloskowska, Chojnacki, Konitz *et al.*, 2006) dissolved in toluene (5 ml) to a suspension of MeONa (1 g, 18.5 mmol) in methanol (10 ml). The raw product which precipitated was recrystallized from toluene. Good quality crystals of (I) (m.p. 403 K) were obtained in moderate yields, with consistent elemental analyses for C, H and S.

Crystal data

$[\text{Na}_4(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_4(\text{CH}_4\text{O})_6]$	$V = 2068.1 (9) \text{ \AA}^3$
$M_r = 1402.16$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.126 \text{ Mg m}^{-3}$
$a = 8.298 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 14.988 (3) \text{ \AA}$	$\mu = 0.25 \text{ mm}^{-1}$
$c = 17.932 (4) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\alpha = 101.90 (3)^\circ$	Plate, colourless
$\beta = 99.64 (3)^\circ$	$0.5 \times 0.4 \times 0.2 \text{ mm}$
$\gamma = 103.38 (3)^\circ$	

Data collection

Kuma KM-4 diffractometer	$R_{\text{int}} = 0.033$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25.6^\circ$
Absorption correction: none	3 standard reflections
7983 measured reflections	every 200 reflections
7721 independent reflections	intensity decay: 0.7%
5883 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0991P)^2 + 0.367P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.145$	$(\Delta/\sigma)_{\text{max}} = 0.005$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$
7721 reflections	$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$
412 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

Si1—S1	2.0559 (10)	Na1—O11	2.871 (2)
Si2—S2	2.0434 (13)	Na1—Na2	3.5906 (16)
S1—Na1	2.7386 (15)	Na2—O12	2.273 (2)
S2—Na1	2.7632 (13)	Na2—O11	2.347 (2)
S2—Na2	2.8542 (13)	Na2—O10 ⁱ	2.405 (2)
Na1—O4	2.362 (2)	Na2—O10	2.420 (2)
Na1—O2	2.3778 (19)	Na2—Na2 ⁱ	3.663 (2)
Si1—S1—Na1	82.51 (4)	O12—Na2—O11	144.91 (9)
O4—Na1—O2	127.76 (7)	O12—Na2—O10 ⁱ	111.68 (9)
O4—Na1—S1	146.61 (6)	O11—Na2—O10 ⁱ	103.36 (8)
O2—Na1—S1	69.40 (5)	O12—Na2—O10	83.08 (8)
O4—Na1—S2	69.88 (5)	O11—Na2—O10	100.85 (8)
O2—Na1—S2	116.42 (6)	O10 ⁱ —Na2—O10	81.23 (8)
S1—Na1—S2	133.13 (4)	O12—Na2—S2	92.68 (6)
O4—Na1—O11	82.81 (7)	O11—Na2—S2	83.93 (6)
O2—Na1—O11	148.80 (7)	O10 ⁱ —Na2—S2	98.31 (6)
S1—Na1—O11	81.10 (5)	O10—Na2—S2	175.19 (6)
S2—Na1—O11	76.74 (5)		

Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O10—H10D \cdots S1 ⁱ	0.78 (4)	2.44 (4)	3.216 (2)	172 (4)
O11—H11D \cdots O5	0.83 (3)	1.99 (3)	2.803 (3)	163 (3)
O12—H12D \cdots S1 ⁱ	0.81 (4)	2.35 (4)	3.161 (2)	175 (4)

Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

Carbon-bound H atoms were placed in idealized positions, with C—H = 0.98 Å, and refined as riding, with $U_{iso}(H) = 1.5U_{eq}(C)$. The

hydroxy H atoms of the methanol ligands were found in a Fourier difference map and refined without constraints (refined O—H distances are in Table 2).

Data collection: *KM-4 Software* (Galdecki *et al.*, 1996); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; 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).

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