

A study of chirality in bis(1,2-dimethoxyethane- κ^2O,O')sodium bis(tri-*tert*-butoxysilanethiolato- κ^2O,S)sodate

Jaroslav Chojnacki,* Anna Ciborska and Wieslaw Wojnowski

Chemical Faculty, Gdansk University of Technology, Narutowicza 11/12, Gdansk PL-80952, Poland

Correspondence e-mail: jaroslav.chojnacki@chem.pg.gda.pl

Received 10 May 2008

Accepted 20 May 2008

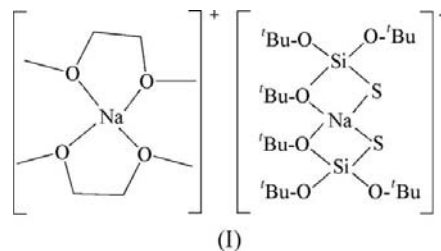
Online 28 May 2008

This work presents an analysis of self-assembly of a complex molecule from simpler ions, some of which are asymmetric, and is an example of a sodium silanethiolate. The tri-*tert*-butoxysilanethiolate anion has two helical conformers (*P* and *M*), so aggregation of silanethiolates can proceed with recognition of chirality. Alkali metal silanethiolates can form cyclic solvated oligomers (*e.g.* dimers) or complexes such as sodates with anions of general formula R_2Na^- . We note that all known sodates (and lithiates) contain both ligands of the same helicity in the anion, whereas in the dimers the metal atoms are coordinated by silanethiolate ligands of different helicity. The title compound, a new example of a sodate, $[Na(C_4H_{10}O_2)_2][Na(C_{12}H_{27}O_3SSi)_2]$ or $[Na\{('BuO)_3SiS\}_2][Na(DME)_2]$ (DME is 1,2-dimethoxyethane), is built up of separate ion pairs with no significant interactions. The anion is formed from an Na atom *O,S*-chelated by two silanethiolate ligands of the same helicity (both *P* or both *M*), while the cation contains an Na atom solvated by two DME molecules. Because the structure is centrosymmetric, equal numbers of both conformational enantiomers are present in the crystal lattice.

Comment

Structural studies of thiolates of the *s*-block elements are important because the compounds often serve as starting materials in inorganic and organic syntheses (Englich & Ruhlandt-Senge, 2000). These complexes form a great variety of solid-state structures (Chadwick *et al.*, 1997; Kückmann *et al.*, 2005). In our scientific research, we have made use of the thiolate ligand $(^tBuO)_3SiS^-$, which was first described by Piękoś & Wojnowski (1962). The only alkali metal tri-*tert*-butoxysilanethiolates known to date have been reported in four papers (Baranowska *et al.*, 2002; Jesionka *et al.*, 2005; Kloskowska *et al.*, 2006*a,b*). We present here the synthesis,

characterization and molecular structure of a new type of sodium tri-*tert*-butoxysilanethiolate, the title compound, $[Na\{('BuO)_3SiS\}_2][Na(DME)_2]$ (DME is 1,2-dimethoxyethane), (I). Some attention is focused on the chirality of the $(^tBuO)_3SiS$ ligand.



Compound (I) is built up of ions combined in pairs in such a way that the outside of the pair is hydrophobic, *i.e.* only alkyl groups are present on the surface. The anionic fragment is formed by an Na atom coordinated by two *O,S*-chelating $(^tBuO)_3SiS$ groups. Both groups have *S—Si—O—C* torsion angles of the same sign (Table 1). The Na atom in the cation is coordinated by two DME molecules (Fig. 1). The distances of atoms S1 and S2 from atom Na1 (inside the anion) are shorter by *ca.* 0.2 Å than those involving Na2 (inside the cation), and therefore the compound is not regarded as a dinuclear complex but as an ion pair. We interpret the Na1—S1 and Na1—S2 distances as bonds and Na2...S1 and Na2...S2 as intermolecular contacts. Both Na atoms are four-coordinate in the first coordination sphere. Naturally, the borderline between a long-separated ion pair and a loosely bound dinuclear complex is quite fuzzy. The other bond lengths are

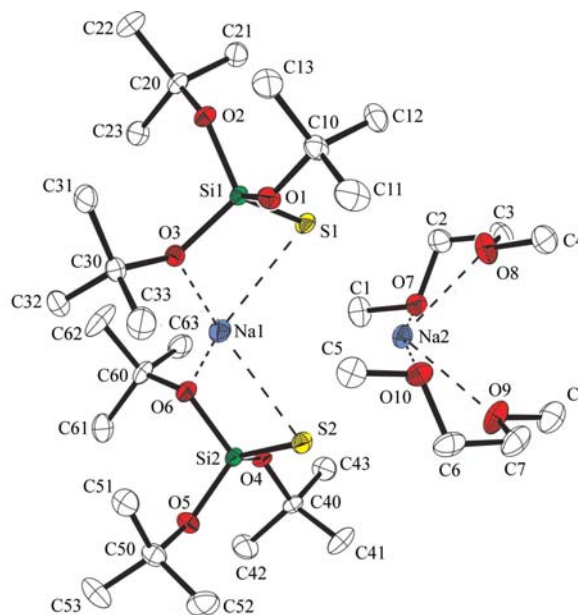


Figure 1

A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity

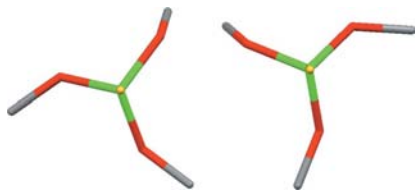


Figure 2

The *M* (left) and *P* (right) conformers of the tri-*tert*-butoxysilanethiolate group, viewed along the S—Si bond. Only S, Si, O and the central *tert*-butyl C atoms are shown.

typical for sodium silanethiolates (*c.f.* Kloskowska *et al.*, 2006*b*). Nevertheless, asymmetry of the silanethiolate ligand also seems to be important in the manner described below.

Both ligands in the anion have a positive chiral sense (helicity) (Table 1 and Fig. 2). This means that, due to steric hindrance, the tri-*tert*-butoxysilanethiolate groups cannot adopt uniform values for all three S—Si—O—C torsion angles. This causes the three *tert*-butoxy groups to be twisted, generating helicity of the ligand (Fig. 2). Because the asymmetry is induced by three chemically identical *tert*-butoxy groups we cannot use simple *R* and *S* notation. Thus, we will apply helicity notation, *P* and *M*. When all the above-mentioned torsion angles are positive, we will call the conformation 'plus' (*P*), and when they are all negative, we will call it 'minus' (*M*). It seems geometrically justified that two right-handed ligands fit better, if they have to be coordinated to the same metal atom. Of course, because the structure is centrosymmetric, the other equivalent reflected by a symmetry centre contains both ligands in a left-handed configuration (*M*). We note that usually the S—Si—O—C torsion angle involving the O atom coordinated to the metal atom is close to 170°.

Interestingly, both previously reported lithium silanethiolates (Jesionka *et al.*, 2005) form centrosymmetric dimers and obviously contain *P* and *M* configurations of the tri-*tert*-butoxysilanethiolate group in each $\text{Li}_2(\text{SR})_2(\text{L})_2$ ring (*L* = tetrahydrofuran or DME).

A complex with a similar structure to (I) was recently obtained, namely $[\text{Na}_2(\text{MeOH})_6][\text{Na}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2]$ (Kloskowska *et al.*, 2006*a*). This compound differs mainly in the form of the cation and in its hydrogen bonds. The use of methanol, a monodentate solvent which can give rise to many hydrogen bonds, results in the structure being a tetranuclear complex with all Na atoms pentacoordinated. This observation suggests that the coordination and hydrogen-bond formation capabilities of the solvent are strong structure-forming factors, which is not surprising. It is noteworthy that both $\text{SSi}(\text{O}^t\text{Bu})_3$ groups are of the same chirality in the anionic fragment $[\{(M)\text{-}(\text{O}^t\text{Bu})_3\text{Si}\}\text{Na}\{(M)\text{-}\text{SSi}(\text{O}^t\text{Bu})_3\}]^-$ of the molecule (or $[\{(P)\text{-}(\text{O}^t\text{Bu})_3\text{Si}\}\text{Na}\{(P)\text{-}\text{SSi}(\text{O}^t\text{Bu})_3\}]^-$), exactly as in compound (I). The same holds for the anion in the lithiate $[\text{Li}_2(\text{D}_2\text{O})_6][\text{Li}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2]\cdot 2\text{H}_2\text{O}$ (Kloskowska *et al.*, 2006*b*).

It seems that analysis of the chirality of $\text{SSi}(\text{O}^t\text{Bu})_3$ fragments gives a new and useful perspective for the analysis of the solid-state structures of tri-*tert*-butoxysilanethiolates.

Experimental

All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. The title compound was synthesized by direct reaction of metallic sodium with $(^t\text{BuO})_3\text{SiSH}$ (Piękoś & Wojnowski, 1962) dissolved in 1,2-dimethoxyethane (DME). The resulting mixture was refluxed for 5 h. Recrystallization of the resulting white precipitate from DME afforded colourless crystals of (I) suitable for X-ray diffraction analysis. Elemental analysis is consistent with the formula $\text{C}_{32}\text{H}_{74}\text{Na}_2\text{O}_{10}\text{S}_2\text{Si}_2$.

Crystal data

$[\text{Na}(\text{C}_4\text{H}_{10}\text{O}_2)_2][\text{Na}(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_2]$	$V = 4660.4$ (5) Å ³
$M_r = 785.19$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 15.5007$ (9) Å	$\mu = 0.23$ mm ⁻¹
$b = 17.4385$ (9) Å	$T = 100$ (2) K
$c = 17.2438$ (12) Å	$0.37 \times 0.25 \times 0.21$ mm
$\beta = 91.003$ (5)°	

Data collection

Oxford Diffraction KM-4-CCD diffractometer	10852 independent reflections
28206 measured reflections	9706 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	455 parameters
$wR(F^2) = 0.109$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.41$ e Å ⁻³
10852 reflections	$\Delta\rho_{\text{min}} = -0.24$ e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Na1—S1	2.7172 (9)	Na2...S2	2.9281 (8)
Na1—S2	2.7765 (9)	Na2—O10	2.3965 (15)
Na1—O6	2.3070 (14)	Na2—O7	2.4012 (14)
Na1—O3	2.3542 (14)	Na2—O8	2.4116 (15)
Na2...S1	2.9431 (8)	Na2—O9	2.4368 (16)
S1—Si1—O1—C10	78.80 (15)	S2—Si2—O4—C40	77.90 (15)
S1—Si1—O2—C20	44.48 (15)	S2—Si2—O5—C50	41.41 (16)
S1—Si1—O3—C30	169.69 (13)	S2—Si2—O6—C60	167.71 (13)

All H atoms (methyl and methylene) were refined as riding, with C—H distances of 0.98 and 0.99 Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was carried out with financial support from the Polish State Committee (grant No. 3T09A12028).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3075). Services for accessing these data are described at the back of the journal.

References

- Baranowska, K., Chojnacki, J., Wojnowski, W. & Krossing, I. (2002). *Acta Cryst.* **E58**, m569–m570.
- Chadwick, S., Englich, U. & Ruhlandt-Senge, K. (1997). *Organometallics*, **16**, 5792–5803.
- Englich, U. & Ruhlandt-Senge, K. (2000). *Coord. Chem. Rev.* **21**, 135–179.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Jesionka, E., Ciborska, A., Chojnacki, J. & Wojnowski, W. (2005). *Acta Cryst.* **C61**, m321–m323.
- Kloskowska, M., Chojnacki, J., Wojnowski, W. & Becker, B. (2006a). *Acta Cryst.* **E62**, m2476–m2478.
- Kloskowska, M., Chojnacki, J., Wojnowski, W. & Becker, B. (2006b). *Acta Cryst.* **C62**, m541–m544.
- Kückmann, T. I., Hermsen, M., Bolte, M., Wagner, M. & Lerner, H.-W. (2005). *Inorg. Chem.* **44**, 3449–3458.
- Oxford Diffraction (2005). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171. Oxford Diffraction Ltd, Abingdon, England.
- Piękoś, R. & Wojnowski, W. (1962). *Z. Anorg. Allg. Chem.* **318**, 212–216.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.