

Triaquabis(tri-*tert*-butoxysilanethiolato)barium

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Key indicators

Single-crystal X-ray study
 T = 100 K
 Mean $\sigma(C-C)$ = 0.013 Å
 R factor = 0.068
 wR factor = 0.174
 Data-to-parameter ratio = 19.5

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

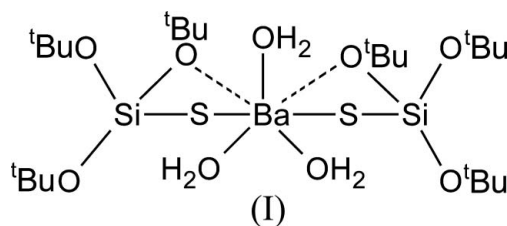
The reaction of metallic barium with tri-*tert*-butoxysilanethiol in the presence of traces of water gives the title compound, $[Ba(C_{12}H_{27}O_3SSi)_2(H_2O)_3]$. The Ba atom is coordinated by two *O,S*-chelating silanethiolate ligands and three water O atoms, forming an intermolecular net of hydrogen bonds of the O—H···O and O—H···S types.

Received 13 July 2006
 Accepted 19 July 2006

Comment

The chemistry of alkaline-earth metal chalcogenates has received little attention, despite their potential use in a number of technical applications such as the production of wide band gap semiconductors (Kondo *et al.*, 1994) or two-colour IR optical windows (Kumta & Risbud, 1994; Lowe-Ma *et al.*, 1995). Only a few structures of heavier alkaline-earth thiolates, selenolates or tellurolates have been reported to date (Henke & Atwood, 1998; Henke *et al.*, 2001; Chadwick *et al.*, 1998; Ruhlandt-Senge, 1997; Ruhlandt-Senge & English, 2000).

The structure and chemistry of silanethiolates have been a subject of research for about 20 years (Wojnowski *et al.*, 1985; Becker *et al.*, 1990; Preuss *et al.*, 1990; Peters *et al.*, 1997; Kovacs *et al.*, 2000; Komuro *et al.*, 2003). Most of the papers describe silanethiolates of transition metals (*e.g.* Becker, Dołęga *et al.*, 2001; Becker, Zalewska *et al.*, 2001) and of the *p*-block elements (Peters *et al.*, 1998; Chojnacki *et al.*, 2001). There are only a few structural reports of silanethiolates of the *s*-block elements (Baranowska *et al.*, 2002; Jesionka *et al.*, 2005) and none to date of alkaline-earth silanethiolates. We present here the structure of the title compound, (I), the first silanethiolate of an alkaline-earth element.



Compound, (I) was obtained by the reaction of metallic barium with tri-*tert*-butoxysilanethiol under evolution of gaseous hydrogen. It should be emphasized that under rigorous anhydrous conditions no crystalline product was formed. Traces of water, which must have entered the system during the various manipulations, are necessary for crystallization, giving a hydrated product.

Compound (I) (Fig. 1) consists of electrically neutral mononuclear complex molecules with a seven-coordinate Ba

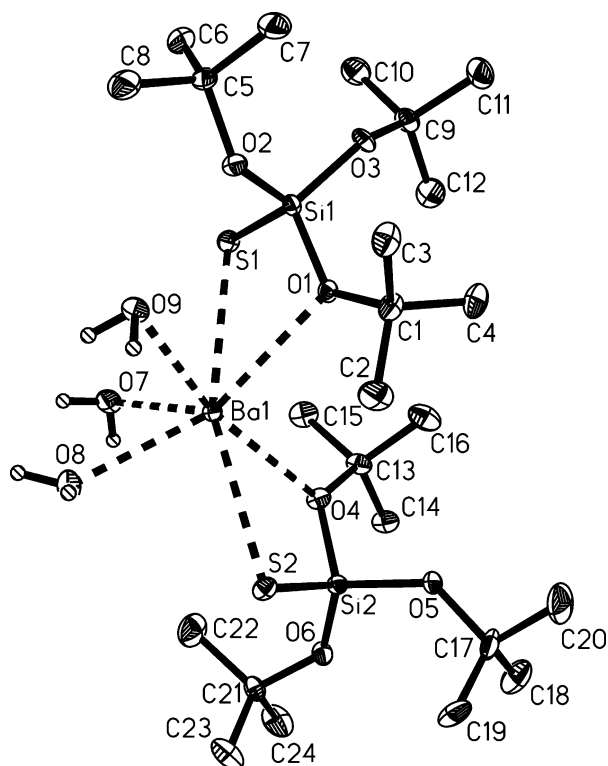


Figure 1
A view of (I), with 50% probability displacement ellipsoids. Thick dashed lines denote coordination bonds.

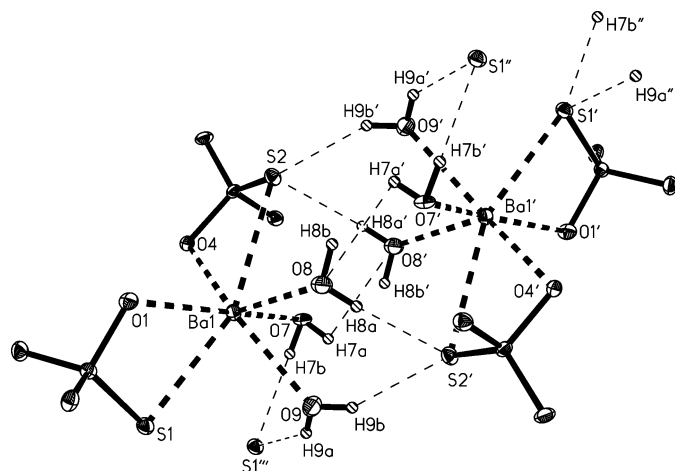


Figure 2
The hydrogen-bonding system in (I). Thick dashed lines denote coordination bonds, thin dashed lines hydrogen bonds. *tert*-Butoxy groups have been omitted. Primed atoms are at the symmetry position $(-x, 1 - y, -z)$, double primed atoms are at the symmetry position $(-1 + x, y, z)$ and triply primed atoms are at the symmetry position $(1 - z, 1 - y, -z)$.

centre. The coordination polyhedron is formed by two S atoms, two O atoms from two chelating silanethiolate ligands, and three O atoms from coordinated water molecules. These silanethiolate ligands are oriented approximately opposite each other, the S—Ba—S valence angle being $158.51(5)^\circ$. The two Ba—S bond lengths are different [Ba1—S1 = $3.1576(19)$

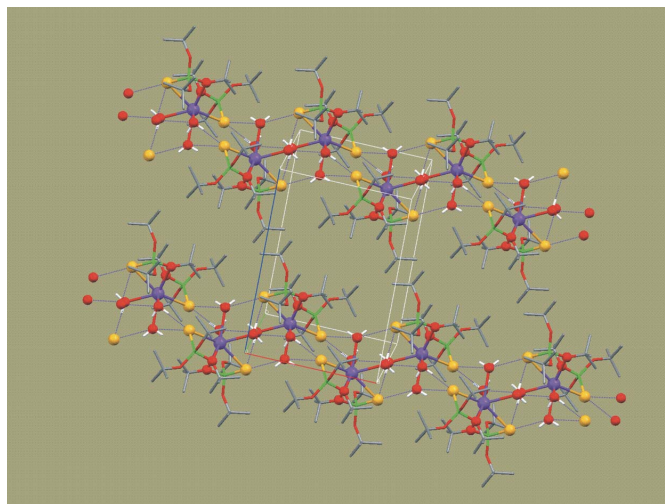


Figure 3
A packing diagram for (I). H atoms attached to C atoms have been omitted for clarity.

and Ba1—S2 = $3.223(2) \text{ \AA}$]. The departure from linearity of the S—Ba—S system is probably forced by the asymmetrical coordination of Ba by water molecules. The contacts between Ba and the chelating O atoms are $2.831(5)$ and $2.923(5) \text{ \AA}$ for atoms O1 and O4, respectively. The Ba—O coordination bond lengths to the water molecules vary from $2.697(5)$ to $2.800(5) \text{ \AA}$. The Si—S bond lengths in (I), $2.063(3)$ and $2.067(3) \text{ \AA}$, are considerably shorter than the relevant distances found in covalent silanethiolates and are comparable with Si—S bonds in ionic silanethiolates.

The presence of the three water molecules enables the formation of intermolecular hydrogen bonds, of the O—H...O and O—H...S types (Table 1, Fig. 2). These intermolecular hydrogen bonds link the molecules of barium silanethiolate to give chains parallel to the *a* axis (Fig. 3). This compound is an example of a macromolecular system in which monomeric units are linked by hydrogen bonds.

Experimental

The synthesis was carried out using a standard vacuum/N₂ line and Schlenk techniques. $(t\text{-BuO})_3\text{SiSH}$ was prepared according to the literature (Piękoś & Wojnowski, 1962). The solvents were dried by standard methods and distilled under argon prior to use. Elemental analysis was performed on an Elemental Analyser EA 1108 (Carlo Erba Instruments).

For the preparation of triaquabis(tri-*tert*-butoxysilanethiolato)-barium, (I), an excess of metallic barium was added to tri-*tert*-butoxysilanethiol (5 ml, 16.5 mmol). The mixture was stirred and heated at 333 K for one week, yielding a white precipitate. The precipitate was washed with a small amount (*ca* 2 ml) of hexane and dissolved in toluene (10 ml). The solution was separated from the excess of metal by filtration. The solvent was removed and the white precipitate was dried under vacuum. The final product, in the form of colourless crystals, was obtained by slow evaporation of a hexane solution. Elemental analysis (calculated for $\text{C}_{24}\text{H}_{60}\text{BaO}_9\text{S}_2\text{Si}_2$): C 38.1 (38.4), H 7.9 (8.1), S 8.3 (8.5)%.

Crystal data

[Ba(C₁₂H₂₇O₃SSi)₂(H₂O)₃]
M_r = 750.36
 Triclinic, *P* $\bar{1}$
a = 10.657 (2) Å
b = 14.412 (3) Å
c = 14.699 (3) Å
 α = 62.88 (3)°
 β = 88.32 (3)°
 γ = 72.02 (3)°
V = 1894.6 (10) Å³
Z = 2
D_x = 1.315 Mg m⁻³
 Mo *K*α radiation
 μ = 1.26 mm⁻¹
T = 100 (2) K
 Needle, colourless
 0.35 × 0.08 × 0.08 mm

Data collection

Kuma KM-4-CCD diffractometer
 ω scans
 Absorption correction: numerical
 [SCALE3 in *CrysAlis RED*
 (Oxford Diffraction, 2005), based
 on algorithms by Clark & Reid
 (1998)]
T_{min} = 0.770, *T_{max}* = 0.928
 13908 measured reflections
 7415 independent reflections
 6598 reflections with *I* > 2σ(*I*)
R_{int} = 0.055
 θ_{max} = 26°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.068
wR(*F*²) = 0.174
S = 1.11
 7415 reflections
 380 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0623P)^2 + 24.8951P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 4.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -1.14 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O7—H7A...O6	0.92 (5)	1.97 (6)	2.843 (7)	159 (10)
O7—H7B...S1 ⁱ	0.92 (5)	2.29 (5)	3.184 (5)	167 (10)
O8—H8A...S2 ⁱⁱ	0.91 (5)	2.41 (11)	3.309 (6)	170 (10)
O9—H9A...S1 ⁱ	0.91 (5)	2.44 (8)	3.226 (6)	144 (9)
O9—H9B...S2 ⁱⁱ	0.91 (5)	2.39 (7)	3.222 (6)	151 (10)

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

H atoms attached to C atoms were positioned geometrically and refined as riding, with C—H = 0.98 Å and *U_{iso}*(H) = 1.2 *U_{eq}*(C). Water H atoms were found in a difference Fourier synthesis and refined with O—H distances restrained to 0.91 (5) Å and with *U_{iso}*(H) = 0.05 Å². The maximum electron-density peak is located 0.91 Å from the Ba atom and the deepest hole 0.82 Å from the same atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduc-

tion: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Financial support for EJ from the Polish Ministry of Research and Information (project Nos. 3 T09A 150 27 and T09A 120 28) is gratefully acknowledged.

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