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Key indicators

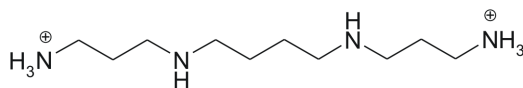
Single-crystal X-ray study
 $T = 200\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
Disorder in main residue
 R factor = 0.035
 wR factor = 0.131
Data-to-parameter ratio = 13.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Sperminium bis(tri-*tert*-butoxysilane-thiolate)–2-propanol (1/2)

The title compound, $\text{C}_{10}\text{H}_{28}\text{N}_4^{2+} \cdot 2\text{C}_{12}\text{H}_{27}\text{O}_3\text{Si}^- \cdot 2\text{C}_3\text{H}_8\text{O}$, has been obtained by the reaction of $(t\text{-BuO})_3\text{SiSH}$ with spermine in the presence of 2-propanol. The sperminium cation sits on an inversion centre at the mid-point of the central C–C bond. The three species are linked together in infinite chains, mainly by $\text{N}-\text{H} \cdots \text{S}$ hydrogen bonds.

Comment

Until now, spermine, despite its biological importance, has not been structurally characterized by X-ray diffraction methods. Only three structures containing the spermine residue can be found in the Cambridge Structural Database (Version 5.24, updates 1–3; Allen, 2002). These are complex salts with copper(II) perchlorate (Boggs & Donohue, 1975), copper(II) sulfate (Maluszynska *et al.*, 1995) and palladium(II) chloride (Codina *et al.*, 1999).

Our scientific interest has focused recently on $\text{N}-\text{H} \cdots \text{S}$ hydrogen-bond networks. Spermine, being a polyamine, provides a unique opportunity to explore the cooperation of several amino groups in the formation of the overall structure, including self-organization of packing in the crystal lattice. Here, we describe the molecular and crystal structure of the title compound, (I), containing a doubly protonated sperminium salt with a bulky *tert*-butoxysilanethiolate anion and two solvent molecules of 2-propanol.



(I)

The asymmetric unit of (I) consists of one tri-*tert*-butoxysilanethiolate anion, one-half sperminium cation and one 2-propanol molecule. The sperminium cation sits on an inversion centre at the mid-point of the central C–C bond, at Wyckoff position h ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). The ions are linked in infinite chains. The two terminal ammonium groups of the sperminium cation form $\text{N}-\text{H} \cdots \text{S}$ hydrogen bonds, each $-\text{NH}_3^+$ group with one thiolate anion. This leads to the graph-set motif $R_4^2(8)$ (Etter, 1990), the centre of which lies on the inversion centre at $(0, 0, \frac{1}{2})$, *i.e.* Wyckoff position b .

The molecule of 2-propanol in (I) accepts one H atom from a non-terminal N atom, forming an $\text{N}-\text{H} \cdots \text{O}$ hydrogen bond. Simultaneously, its OH group behaves as a donor to form an $\text{O}-\text{H} \cdots \text{S}$ hydrogen bond. The S atom forms an $\text{S} \cdots \text{H}-\text{N}$ bond with the terminal $-\text{NH}_3^+$ group. Additionally, each

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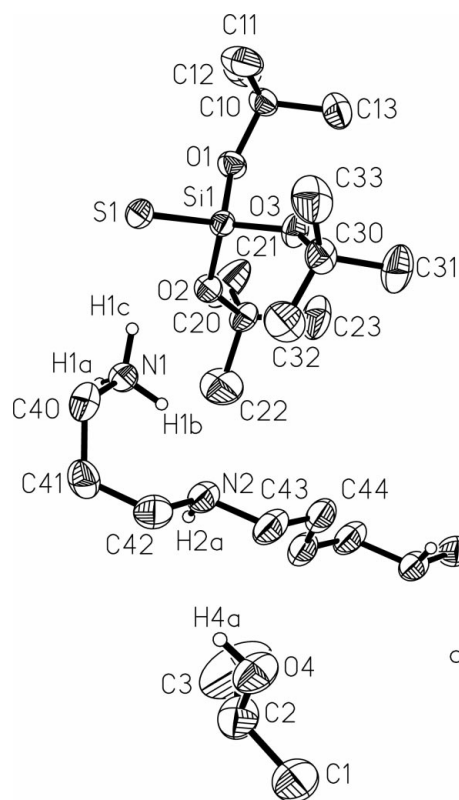


Figure 1

The molecular structure of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms bonded to C atoms have been omitted for clarity. The asymmetric unit is shown, together with the other half of the cation. Only one component of the disordered tert-butyl group is included

terminal ammonium group forms an intramolecular N—H···N hydrogen bond with one non-terminal amine group. These interactions may be described as a set of first-level graphs $C(3)$, $C(3)$, $C(3)$, $S(6)$, or, taken together, as the graph-set motif $R_4^3(8)$ [adjacent to the above-mentioned N—H···S $R_4^2(8)$ motif].

The S···N distances in (I) lie in the range 3.262 (3)–3.265 (3) Å, comparable with values observed in dicyclohexylammonium benzenethiolate (Baranowska *et al.*, 2003), as well as in zinc and cobalt benzenethiolate complexes (Chung *et al.*, 1991a,b).

Experimental

All synthetic procedures were carried out under argon, using standard Schlenk techniques. Tri-*tert*-butoxysilanethiol (Piekos & Wojnowski, 1962) was prepared according to literature procedures. Solvents were dried by standard methods and distilled under argon prior to use. (tBuO)₃SiSH (3 mmol) was added to a solution of spermine (120 mg, 0.6 mmol) [NH₂(CH₂)₃NH(CH₂)₄NH(CH₂)₃NH₂] in toluene (10 ml). On allowing the solution to stand for *ca* one week at 273–278 K, small transparent crystals were formed. These were collected and recrystallized from 2-propanol, giving small crystals of (I) of good quality, with a sharp m.p. of 357–358 K. Analysis found: C 53.6, H 10.9, N 7.2, S 8.3%; calculated for C₁₇H₄₁N₂O₃SSi: C 53.5,

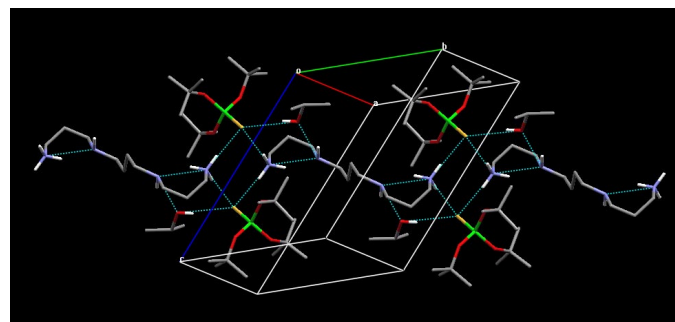


Figure 2

A packing diagram for (I), showing the hydrogen-bond network.

H 10.8, N 7.3, S 8.4%. This result indicates loss of 2-propanol during drying.

Crystal data

C₁₀H₂₈N₄²⁺·2C₁₂H₂₇O₃SSi⁻·
2C₃H₈O
M_r = 883.52
Triclinic, $P\bar{1}$
a = 9.419 (2) Å
b = 12.970 (3) Å
c = 13.525 (3) Å
 α = 102.08 (3)°
 β = 108.64 (3)°
 γ = 109.65 (3)°
V = 1378.4 (8) Å³

Z = 1
D_x = 1.064 Mg m⁻³
Mo *K*α radiation
Cell parameters from 65 reflections
 θ = 5.9–31.9°
 μ = 0.19 mm⁻¹
T = 200 (2) K
Block, colourless
0.40 × 0.30 × 0.20 mm

Data collection

Kuma KM-4 diffractometer
 $\omega/2\theta$ scans
Absorption correction: none
4475 measured reflections
4254 independent reflections
2954 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

θ_{\max} = 25.0°
h = −10 → 10
k = 0 → 14
l = −15 → 15
3 standard reflections
every 200 reflections
intensity decay: 0.8%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)]$ = 0.035
 $wR(F^2)$ = 0.131
S = 1.00
4254 reflections
310 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0913P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Si1—Si1	2.0657 (12)	N1—C40	1.479 (3)
Si1—O1	1.6302 (18)	C42—N2	1.472 (4)
Si1—O3	1.6312 (19)	N2—C43	1.469 (3)
Si1—O2	1.6418 (17)		
O1—Si1—Si1	115.78 (7)	N2—C42—C41	111.5 (2)
O3—Si1—Si1	114.98 (8)	C43—N2—C42	110.6 (2)
O2—Si1—Si1	105.90 (7)	N2—C43—C44	113.5 (2)
N1—C40—C41	112.0 (2)	C43—C44—C44 [†]	114.7 (3)
C40—C41—C42	114.5 (2)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots S1 ⁱⁱ	0.87 (3)	2.41 (3)	3.265 (3)	167 (3)
N1—H1B \cdots N2	0.93 (3)	2.09 (3)	2.887 (3)	144 (3)
N1—H1C \cdots S1	0.98 (3)	2.30 (3)	3.262 (3)	169 (3)
N2—H2A \cdots O4 ⁱⁱⁱ	0.87 (3)	2.46 (3)	3.239 (3)	150 (3)
O4—H4A \cdots S1 ^{iv}	0.84 (3)	2.48 (3)	3.301 (2)	167 (3)

Symmetry codes: (ii) $-x, -y, 1-z$; (iii) $x-1, y, z$; (iv) $1-x, -y, 1-z$.

The data are 88% complete. Measurements were not complete because, after 4–5 d, there were technical problems with icing. Reflections in the high- θ region were of poor quality. H atoms attached to N and O atoms were refined freely, whereas those attached to C atoms were refined with a riding model. C—H distances were set to 0.98 (methyl H), 0.99 (methylene H) and 1.00 Å (methine H). $U_{\text{iso}}(\text{H})$ values were constrained to be 1.2 (1.5 for methyl and methine H) times U_{eq} of the carrier atom. Atoms C21–C23 of one *tert*-butyl group are disordered over two positions with site occupancy factors of 0.628 (9) and 0.372 (9).

Data collection: *KM-4 Software* (Kuma Diffraction, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Galdecki *et al.*, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *RESVIEW* (Schwenk, 1998); software used to prepare material for publication: *SHELXL97*.

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