

Aminosilanetrithiol $\text{RSi}(\text{SH})_3$: an experimental and quantum-chemical study†

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An interesting aminosilanetrithiol $\text{RSi}(\text{SH})_3$ ($\text{R} = \text{N}(\text{SiMe}_3)\text{-2,6-iPr}_2\text{C}_6\text{H}_3$) has been prepared by the reaction of lithium aminosilanetrithiolate $\{\text{RSi}[\text{SLi}(\text{THF})]_3\}_2$ with MeCOOH . Theoretical calculations indicate that the $\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Si-S})$ and $\text{LP}(\text{S}) \rightarrow \sigma^*(\text{Si-S})$ electron donations remarkably contribute to the stabilization of the $\text{Si}(\text{SH})_3$ part of the molecule. $\text{RSi}(\text{SH})_3$ is the first example of a stable molecule containing three SH groups attached to one element.

Orthoformic acid ($\text{HC}(\text{OH})_3$) and its sulfur congener ($\text{HC}(\text{SH})_3$) are hypothetical molecules. Aqueous formic acid possibly contains $\text{HC}(\text{OH})_3$ which is considered to be extremely unstable.¹ The analogous silicon species $\text{HSi}(\text{OH})_3$ and $\text{HSi}(\text{SH})_3$ have also been proposed and theoretically studied.² $\text{RSi}(\text{OH})_3$ compounds with the bulky R substituents ($\text{R} = \text{alkyl, aryl, aryloxy, or aryl-substituted amide group or a metal cluster}$) have already been reported since the 1950s.³ They are extensively employed as building blocks for assembling lipophilic three-dimensional Si-O metal clusters.^{3b-d} However, the sulfur analogue $\text{RSi}(\text{SH})_3$ has not been prepared so far.

It has been documented that some of the triorganosilanethiols (R_3SiSH) and diorganosilanedithiols ($\text{R}_2\text{Si}(\text{SH})_2$) can be obtained by a variety of methods including alcoholysis of SiS_2 ,⁴ protonation of potassium silanethiolate,⁵ insertion of sulfur into triorganosilane,⁶ treatment of silylsulfide with hydrogen halide,⁷ and LiAlH_4 reduction of a silanepolysulfide.⁸ More recently, a transition metal-trapped silylenylthiol $\text{LSi}[\text{Ni}(\text{CO})_3]\text{SH}$ ($\text{L} = \text{HC}[\text{C}(\text{Me})\text{CN-2,6-iPr}_2\text{C}_6\text{H}_3]_2$) has been achieved by 1,4-addition of H_2S to $\text{L}'\text{Si}[\text{Ni}(\text{CO})_3]$ ($\text{L}' = \text{HC}[\text{C}(\text{Me})\text{N-2,6-iPr}_2\text{C}_6\text{H}_3][\text{C}(\text{CH}_2\text{N-2,6-iPr}_2\text{C}_6\text{H}_3)]$).⁹ In comparison

with the preparation of the organosilanols,³ the synthesis of the organosilanethiols appears to be more complex. The approach to prepare organosilanetrithiol by reacting the $\text{R}'\text{SiCl}_3$ ($\text{R}' = \text{Me}_2\text{iPrC}$ or Me) precursor with Li_2S^{10} or $\text{H}_2\text{S}/\text{NET}_3$ in the presence of $\text{MeCl}_2\text{Si-SiCl}_2\text{Me}^{11}$ was not successful, and instead the silylsulfide clusters $((\text{Me}_2\text{iPrCSi})_4\text{S}_6$ and $(\text{MeSi})_4\text{S}_5$) were produced. An intermediate in these reactions might be the Si-S-M ($\text{M} = \text{Li, H}$) moiety, which further reacted to yield the Si-S-Si unit observed in the clusters.

$\text{RSi}(\text{OH})_3$ has been prepared by using RSiCl_3 with a bulky R group which prevents the condensation shown in the previous work.^{3c} Following the strategy of synthesizing $\text{RSi}(\text{OH})_3$ by controlled hydrolysis of RSiCl_3 (**1**, $\text{R} = \text{N}(\text{SiMe}_3)\text{-2,6-iPr}_2\text{C}_6\text{H}_3$) in the presence of an amine as the HCl-acceptor,¹² we used H_2S instead of H_2O . The experiments were carried out with different amines (NET_3 , $\text{2,6-iPr}_2\text{C}_6\text{H}_3\text{NH}_2$, or pyridine) at various temperatures.¹³ However, no reaction was observed.

Subsequently, we employed a salt metathesis reaction by treating **1** with Na_2S or K_2S , however, according to NMR analysis no transformation occurred. When we used a freshly prepared Li_2S^6 obtained from the reaction of sulfur with LiBET_3H , the reaction proceeded and several products were formed depending on the amount of Li_2S and the reaction conditions. As illustrated in Scheme 1, the reaction of **1** with 5.3 equivalents of Li_2S in THF was carried out at 25 °C and stirred for 10 days, affording $\{\text{RSi}[\text{SLi}(\text{THF})]_3\}_2$ (**2**) as colorless crystals in high yield (85%). However, upon changing the temperature, time, and ratio of the precursors, the reaction only resulted in products $\text{RSiCl}_2\text{SLi}(\text{THF})_3$ (**3**) and $\text{RSi}[\text{SLi}(\text{THF})](\mu\text{-S})_2\text{Si}[\text{SLi}(\text{THF})_2]\text{R}$ (**4**). Compound **3** is an incompletely sulfurized species which can be isolated as colorless crystals in 80% yield, when the reaction was conducted under stirring at 10 °C for 24 h using three equivalents of Li_2S . Increasing the reaction temperature to 35 °C and extending the reaction time to 72 h yielded a mixture of **3** and **4**. The latter shows the formation of a $\text{Si}(\mu\text{-S})_2\text{Si}$ moiety, which is generated at a little higher temperature than 25 °C and is not observed during the formation of **2**. Compared with the results reported in the literature,^{10,11} it is worth noting that a combination of the right RSiCl_3 ,¹⁴ restricted temperature, long reaction time, and excess of Li_2S is important to the successful and high yield production of **2**.

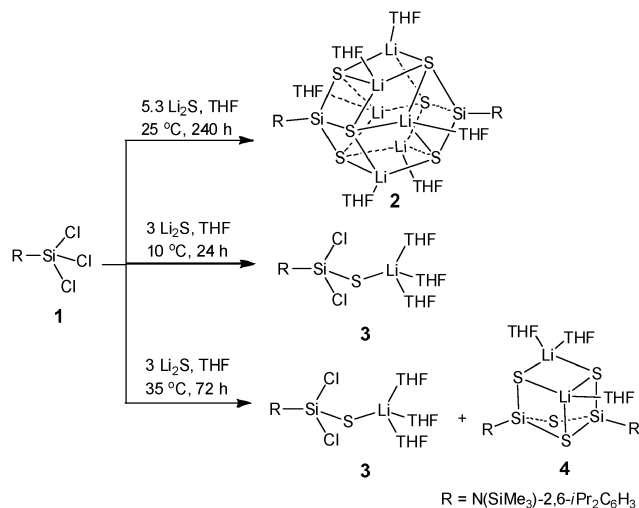
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† Electronic supplementary information (ESI) available: Experimental procedures and X-ray crystallographic and computational information. CCDC 973535 (**2**), 973536 (**3**), 973538 (**4**), 979368 (**5**), and 987309 (**6**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc00912f





Scheme 1 Reaction of **1** with freshly prepared Li_2S under different reaction conditions to produce compounds **2–4**.

Compounds **2–4** are air and moisture sensitive and have been characterized by NMR spectroscopy and X-ray crystallography. Compound **2** shows symmetric patterns in ^1H , ^{13}C and ^{29}Si NMR spectra in solution, indicating that all the R groups in **2** are equivalent. The CHMe_2 resonance (4.05 ppm) of R in **2** is lowfield shifted when compared with those of **3** (3.60 ppm) and **4** (3.43 ppm). The ^{29}Si NMR spectra of **2** display the respective resonances at δ 1.2 (SiMe_3) and -4.2 ppm (SiS). The X-ray single-crystal structural analysis of **2** (Fig. 1) reveals that two $\text{Si}(\text{SLi})_3$ are assembled into a metal cage cluster which is comparable to those of the organosilane-triethiol-derived metallosiloxanes formed.^{3b–d} The rhomboid-based dodecahedral $\text{Si}_2\text{S}_6\text{Li}_6$ core of structure **2** contains six tetra-coordinate Li atoms each linked to one O atom from the THF molecule and three S atoms. Each of the six S atoms is located at the apex of a tetragonal pyramid and a SiLi_3 four-membered ring forms the base of the pyramid. Similar structures containing $\text{Si}_2\text{N}_6\text{Li}_6$,¹⁵ $\text{Si}_2\text{P}_6\text{Li}_6$,¹⁶ and $\text{Ge}_2\text{As}_6\text{Li}_6$ ¹⁷ frameworks have been reported. The congener $\text{RSi}(\text{OX})_3$ (X = alkali metal) has not been prepared so far. The Si–S (2.1098(10)–2.1383(10) Å) and S–Li (2.398(5)–2.528(5) Å) bond

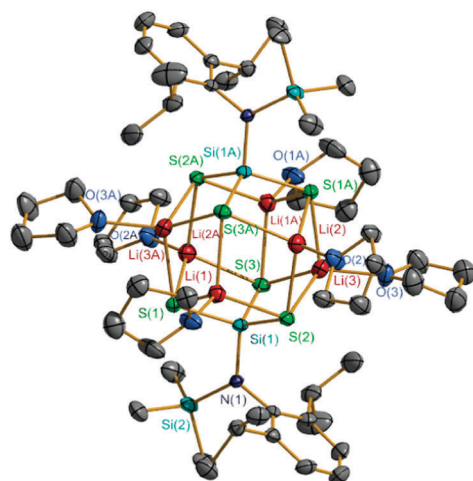
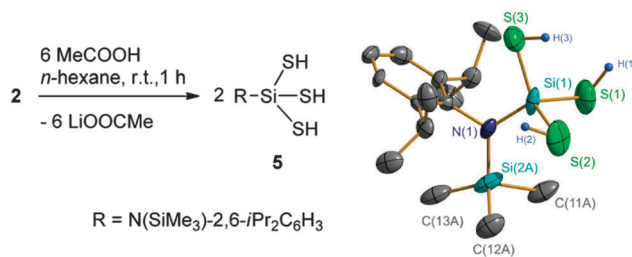


Fig. 1 X-ray crystal structure of **2** with H atoms omitted for clarity.



Scheme 2 Synthesis and the crystal structure of **5**.

lengths in **2** are comparable with those in **3** and **4**, respectively. The X-ray structures and detailed descriptions of **3** and **4** are given in the ESI†

Compound **2** is a potential precursor for preparing aminosilane-trithiol. As expected, treatment of **2** with MeCOOH easily produced $\text{RSi}(\text{SH})_3$ (**5**) as colorless crystals in 40% yield (Scheme 2). The alternative use of CF_3COOH , $\text{C}_6\text{H}_5\text{COOH}$, or $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$ is also possible but does not improve the yield.¹⁸ Compound **5** is air and moisture sensitive. It has a melting point of 154°C , indicative of good thermal stability. In addition, **5** exhibits good solubility in common organic solvents such as *n*-hexane, toluene, diethyl ether, THF, and chlorinated hydrocarbons. The ^1H NMR spectrum of **5** clearly shows the SH proton resonance at δ 1.18 ppm, which is comparable to those found in $\text{Tbt}(\text{Mes})\text{Si}(\text{SH})_2$ and $\text{Tbt}(\text{Mes})\text{Si}(\text{OH})\text{SH}$ (0.87–1.18 ppm).⁸ The SiS silicon resonance (2.7 ppm) is remarkably lowfield shifted even to a positive value in contrast to those of the SiO ones of the organosilane-triols (-40 to -90 ppm).^{3d,13} A strong SH absorption band is observed at $\tilde{\nu}$ 2543 cm^{-1} in the IR spectrum.

The structural analysis unambiguously reveals **5** to be a monomeric molecule (Scheme 2). However, the refinements indicate a severe disorder for the N-bonded SiMe_3 and $\text{Si}(\text{SH})_3$ groups which are pseudo-symmetrically arranged along the N–C_{aryl} axis, although the Me and SH groups show different appearances (see Fig. S4 in the ESI†). Treatment with a splitting mode results in a setting of the related bond lengths (Si–S, $2.10\text{--}2.25 \pm 0.01$; Si–C, 1.86 ± 0.01 ; $\text{Si}_{\text{SiMe}_3}\text{--N}$, 1.76 ± 0.01 ; $\text{Si}_{\text{SiS}}\text{--N}$, 1.72 ± 0.01 ; S–H, 1.35 ± 0.03 Å) on the basis of the reported coordinate data. The final refinement gives convergence with bond parameters (Si–S, $2.101(8)\text{--}2.110(7)$ Å; S–H, $1.31\text{--}1.34(3)$ Å; \angle Si–S–H, $94(4)\text{--}109(2)^\circ$) comparable to those found in $\text{Tbt}(\text{Mes})\text{Si}(\text{SH})_2$, $\text{Tbt}(\text{Mes})\text{Si}(\text{OH})\text{SH}$,⁸ and $\text{LSi}[\text{Ni}(\text{CO})_3]\text{SH}$ ⁹ as well as in the predicted $[\text{Si}(\text{SH})_3]_n^{2a}$

To further understand the bonding matrix of compound **5**, we carried out quantum chemical calculations on the basis of density functional theory (DFT). By optimizing the geometry of the molecule **5** at the M06-2X/def2-TZVPP level,¹⁹ the general structure (Fig. S6, ESI†) calculated is basically in agreement with the results obtained by the X-ray structural analysis (Fig. S4, ESI†). The $\text{Si}_{\text{Si}(\text{SH})_3}\text{--N}$ distance (1.712 Å) is computed to be ca. 0.020 Å longer than the experimental value while the $\text{Si}_{\text{SiMe}_3}\text{--N}$ one (1.774 Å) is 0.014 Å shorter. Both the experimental and theoretical values are significantly shorter than the Si–N standard value (1.87 Å).²⁰ The experimental Si–S bond lengths range from $2.101(8)$ to $2.110(7)$ Å, which are a little shorter than the calculated distances (2.139–2.147 Å).

We also performed the calculation on the ^1H and ^{29}Si NMR spectroscopic data by means of DFT-GIAO calculations.²¹



Since the NMR measurements were carried out in solution (CDCl_3), we optimized the geometry of **5** using the PCM (Polarized Continuum Model)²² method in which the effect by solvent was considered. Therefore, the geometry of **5** optimized at the PCM(CHCl_3)-M06-2X/def2-TZVPP level²² is only slightly different from the one at the M06-2X/def2-TZVPP level. It is computed that the chemical shifts for the $\text{Si}(\text{SH})_3$ group are at δ 2.02 ppm for the proton and 5.97 ppm for the silicon atom. The data for the hydrogen and silicon in the SiMe_3 moiety are at δ 0.35 and 11.25 ppm, respectively. These data generally fit to the experimental^{5,9} and the other related computational data.²³ Furthermore, the computed IR spectrum exhibits a band for the SH groups at $\tilde{\nu}$ 2753 cm^{-1} , which is a little higher than the experimental value.

A natural bond orbital (NBO) analysis²⁴ was accomplished to investigate the bonding situation of **5**. The NBO results identify two N–Si bonds which are strongly polarized toward nitrogen (84% for the N atom and 16% for the Si atoms). The partial charges calculated suggest that the nitrogen atom carries a negative charge ($-1.38 e$) in a large extent while the silicon atoms have strong positive charges, namely, $+1.91 e$ (for SiMe_3) and $+1.46 e$ (for $\text{Si}(\text{SH})_3$). The Wiberg bond order values P for $\text{Si}_{\text{SiS}}-\text{N}$ and $\text{Si}_{\text{SiMe}_3}-\text{N}$ bonds have been calculated at different levels of theory (Table S5, ESI†). The data point out that the former ($P = 0.61\text{--}0.63$) has a higher bond order than the latter ($P = 0.56\text{--}0.58$). The former one can be explained by hyperconjugation of the lone pair orbital of the nitrogen, which is calculated by using a second-order perturbation theory included in the NBO method. The $\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Si}-\text{S})$ donation amounts to 17.8 kcal mol^{-1} while the $\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Si}-\text{C})$ hyperconjugation is only 11.2 kcal mol^{-1} (Table S3, ESI†). Furthermore, application of the second-order perturbation theory revealed delocalization by three stabilizing two-electrons from the sulfur ($\text{LP}(\text{S})$) to the anti-bonding orbital $\sigma^*(\text{Si}-\text{S})$, giving hints of a high conjugation of the $\text{Si}(\text{SH})_3$ fragment. The computed associated energies ($\Delta E(2)$) are 13.54, 12.81 and 11.67 kcal mol^{-1} for each of the $\text{LP}(\text{S}) \rightarrow \sigma^*(\text{Si}-\text{S})$ interactions.

In summary, we have successfully synthesized the amino-silanetrithiol $\text{RSi}(\text{SH})_3$ (**5**) through protonation of its precursor $\{\text{RSi}[\text{SLi}(\text{THF})]_3\}_2$ (**2**) by MeCOOH . Precise control of the reaction conditions is crucial for the synthesis of **2**, while varying the reaction conditions led to the products **3** and **4**. DFT calculations of **5** confirm the experimental data. The corresponding NBO analysis shows that the $\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Si}-\text{S})$ and $\text{LP}(\text{S}) \rightarrow \sigma^*(\text{Si}-\text{S})$ donations remarkably contribute to the stabilization of the $\text{Si}(\text{SH})_3$ fragment. Compound **5** shows a structure containing three SH groups attached to one element. The reactivity studies of **5** are now in progress.²⁵

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- We have tried H_2S in the liquid form at ca. -100°C and allowed it to slowly warm to room temperature in the course of the reaction.
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- Currently, we have obtained some preliminary results by isolating Ag_4 clusters of composition $[\text{R}(\text{HS})_2\text{SiSAg}]_4$ (**6**) and $[\text{R}(\text{HS})_2\text{SiSAg}]_2(\text{AgMes})_2$ (**7**) from the reaction of **5** with $(\text{AgMes})_4$, which indicate a mono-functional reaction of the trithiol (**5**). Due to poor quality of the crystals of **7**, a preliminary structure of this compound was determined. The synthesis of these two compounds and crystallographic data of **6** are included in ESI†.

