

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

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Cite this: *Chem. Commun.*, 2014, 50, 4628

Received 4th February 2014,
Accepted 10th March 2014

DOI: 10.1039/c4cc00912f

www.rsc.org/chemcomm

An interesting aminosilanetrithiol $\text{RSi}(\text{SH})_3$ ($\text{R} = \text{N}(\text{SiMe}_3)\text{-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3$) 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 $\text{LSi}[\text{Ni}(\text{CO})_3]\text{SH}$ ($\text{L} = \text{HC}[\text{C}(\text{Me})\text{CN-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3]_2$) has been achieved by 1,4-addition of H_2S to $\text{L}'\text{Si}[\text{Ni}(\text{CO})_3]$ ($\text{L}' = \text{HC}[\text{C}(\text{Me})\text{N-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3][\text{C}(\text{CH}_2\text{N-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)]$).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 $\text{R}'\text{SiCl}_3$ ($\text{R}' = \text{Me}_2i\text{PrC}$ 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 $((\text{Me}_2i\text{PrCSi})_4\text{S}_6$ 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**, $\text{R} = \text{N}(\text{SiMe}_3)\text{-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3$) 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 , $2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}_2$, 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**.

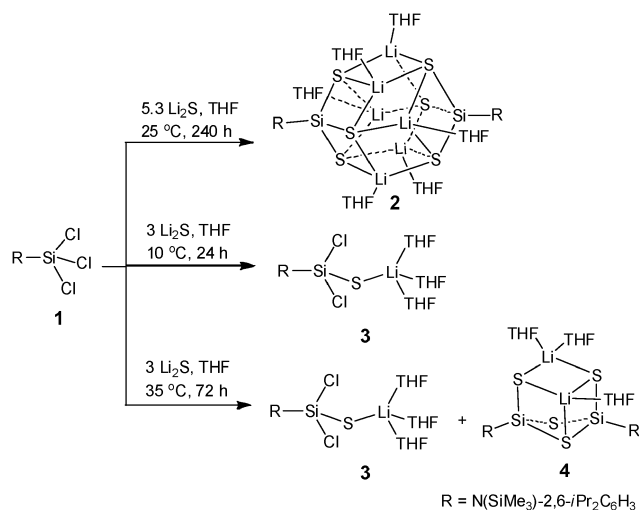
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† Electronic supplementary information (ESI) available: Experimental procedures and X-ray crystallographic and computational information. CCDC 973535 (**2**), 973536 (**3**), 973538 (**4**), 979368 (**5**), and 987309 (**6**). For ESI and crystallographic 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 organosilanetriol-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

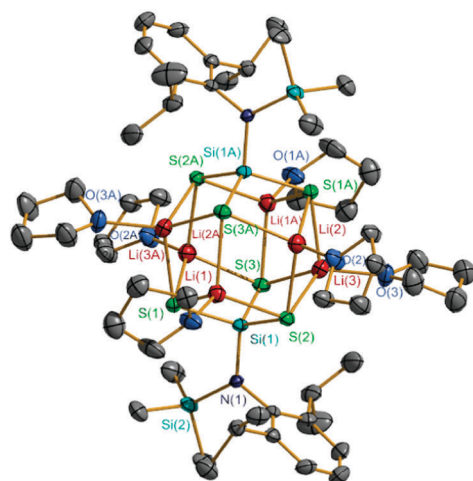
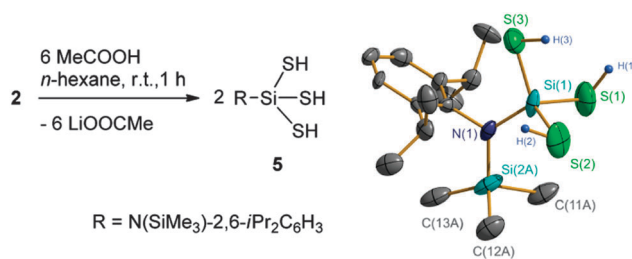


Fig. 1 X-ray crystal structure of **2** with H atoms omitted for clarity.



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 organosilanetriols (-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

This work was supported by the 973 Program (2012CB821704), the National Nature Science Foundation of China (91027014), and the Innovative Research Team Program (IRT1036 and 20923004). Support of the Deutsche Forschungsgemeinschaft (DFG) is highly acknowledged.

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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†.

