Aminosilanetrithiol RSi(SH)₃: an experimental and quantum-chemical study†

Yan Li, a,b Hongping Zhu,* a Diego M. Andrade, c Gernot Frenking,* c and Herbert W. Roesky* b

An interesting aminosilanetrithiol RSi(SH)₃ (R = N(SiMe₃)-2,6-iPr₂C₆H₃) has been prepared by the reaction of lithium aminosilanetrithiololate [RSi(Li(THF))₃]₂ with MeCOOH. Theoretical calculations indicate that the LP(N) → σ*(Si–S) and LP(S) → σ*(Si–S) electron donations remarkably contribute to the stabilization of the Si(SH)₃ part of the molecule. RSi(SH)₃ is the first example of a stable molecule containing three SH groups attached to one element.

Orthoformic acid (H(CO)₂)₃ and its sulfur congener (H(CS)₂)₃ are considered to be extremely unstable. The analogous silicon species HSi(OH)₃ and HSi(SH)₃ have also been proposed and theoretically studied. RSi(OH)₃ compounds with the bulky R substituents (R = alkyl, aryl, arylxoy, or aryl-substituted amide group or a metal cluster) have already been reported since the 1950s. They are extensively employed as building blocks for assembling lipophilic three-dimensional Si-O metal clusters. However, the sulfur analogue RSi(SH)₃ has not been prepared so far.

It has been documented that some of the triorganosilanethiols (R₃SiSH) and diorganosilanedithiols (R₂Si(SH)₂) can be obtained by a variety of methods including alcoholysis of SiS₂, protonation of potassium silanethiolate, insertion of sulfur into triorganosilanes, treatment of silylsulfide with hydrogen halide, and LiAlH₄ reduction of a silanepolysulfide. More recently, a transition metal-trapped silylenylthiol LSi[Ni(CO)₃]SH (L = HC[C(Me)CN-2,6-iPr₂C₆H₃]) has been achieved by 1,4-addition of H₂S to L'Si[Ni(CO)₃] [L’ = HC[C(Me)N-2,6-iPr₂C₆H₃]][C(CH₃)₂N-2,6-iPr₂C₆H₃]. In comparison with the preparation of the organosilanols, the synthesis of the organosilanethiols appears to be more complex. The approach to prepare organosilanethiols by reacting the R’SiCl₃ (R’ = Me,Ph, or Me) precursor with Li₂S or H₂S/NEt₃ in the presence of MeCl₂Si-SiCl₂Me¹¹ was not successful, and instead the silylsulfide clusters ([Me₃SiCl]₂Si and [Me₃Si]₂Si) were produced. An intermediate in these reactions might be the Si–S–M (M = Li, H) moiety, which further reacted to yield the Si–S–Si unit observed in the clusters.

RSi(OH)₃ has been prepared by using RSiCl₃ with a bulky R group which prevents the condensation shown in the previous work. Following the strategy of synthesizing RSi(OH)₃ by controlled hydrolysis of RSiCl₁ (1, R = N(SiMe₃)-2,6-iPr₂C₆H₃) in the presence of an amine as the HCl-acceptor,¹² we used H₂S instead of H₂O. The experiments were carried out with different amines (NEt₃, 2,6-iPr₂C₆H₃NH₂, or pyridine) at various temperatures. However, no reaction was observed.

Subsequently, we employed a salt metathesis reaction by treating 1 with Na₂S or K₂S, however, according to NMR analysis no transformation occurred. When we used a freshly prepared Li₂S obtained from the reaction of sulfur with LiBEt₃H, the reaction proceeded and several products were formed depending on the amount of Li₂S and the reaction conditions. As illustrated in Scheme 1, the reaction of 1 with 5.3 equivalents of Li₂S in THF was carried out at 25 °C and stirred for 10 days, affording [RSi(Si(THF))₂]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 RSiCl₂SiL(Si(THF))₂ (3) and RSi(SiL(Si(THF)))₂SiL(Si(THF))₂R (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 Li₂S. 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 Si[μ-S₂]₂Si 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 RSiCl₃ restricted temperature, long reaction time, and excess of Li₂S is important to the successful and high yield production of 2.
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 $^1$H, $^{13}$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 $\delta$ 1.2 (SiMe$_3$) and $\delta$ 4.2 ppm (SiS). The X-ray single-crystal structural analysis of 2 (Fig. 1) reveals that two Si(SLI)$_3$ are assembled into a metal cage cluster which is comparable to those of the organosilanetriol-derived metallosiloxanes formed.$^{10-12}$ The rhomboid-based dodecahedral Si$_2$S$_6$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$_4$ four-membered ring forms the base of the pyramid. Similar structures containing Si$_4$N$_6$Li$_6^{15}$ Si$_4$P$_6$Li$_6^{16}$ and Ge$_2$As$_6$Li$_6^{17}$ frameworks have been reported.

The congener RSi(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 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 ESL.†

Compound 2 is a potential precursor for preparing aminosilane-trithiol. As expected, treatment of 2 with MeCOOH easily produced RSi(SH)$_3$ (5) as colorless crystals in 40% yield (Scheme 2). The alternative use of CF$_3$COOH, C$_6$H$_5$COOH, or p-MeC$_6$H$_4$SO$_3$H is also possible but does not improve the yield.† 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 $^1$H NMR spectrum of 5 clearly shows the SH proton resonance at $\delta$ 1.18 ppm, which is comparable to those found in Tbt(Mes)Si(SH)$_3$ and Tbt(Mes)Si(OH)SH (0.87–1.18 ppm). The SiS silicon resonance (2.7 ppm) is remarkably lowfield shifted compared with those of the SiO ones of the organosilanetriols (−40 to −90 ppm).$^{14,15}$ 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 Si(SH)$_3$ groups which are pseudo-symmetrically arranged along the N–Caryl 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, 2.10–2.25 Å) comparable to those found in organosilanetriols (−40 to −90 ppm).$^{14,15}$

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,$^{16}$ 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 Si(SH)$_3$–N distance (1.712 Å) is computed to be ca. 0.020 Å longer than the experimental value while the Si(SH)$_3$–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 $^1$H and $^{29}$Si NMR spectroscopic data by means of DFT-GIAO calculations.$^{21}$

![Scheme 2 Synthesis and the crystal structure of 5.](image-url)

Scheme 2 Synthesis and the crystal structure of 5.
Since the NMR measurements were carried out in solution (CDCl₃), 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(CHCl₃)/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 Si(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 SiMe₃ moiety are at δ 0.35 and 11.25 ppm, respectively. These data generally fit to the experimental⁵,⁶ and the other related computational data.²³ Furthermore, the computed IR spectrum exhibits a band for the SH groups at ν 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 SiMe₃) and +1.46 e (for Si(SH))₃. The Wiberg bond order values of Si₃N₅S (for SiMe₃) and Si₃Si₅S₃N (for Si(SH))₃ are 1.38 and 1.46, which are now in progress.²⁵

Carbon–silicon bond lengths of 1.8794 and 1.8811 Å in the compound Si₂N₅S₂ and Si₃N₅S₃, respectively. The remarkable differences in these bond lengths may be related to the structures of these compounds and crystallographic data of similar compounds.¹⁻³ The computed Si(SH)₃ stretching vibration at 2873 cm⁻¹ in the liquid form at ca. 100 °C, which is calculated by using second-order perturbation theory included in the NBO method. The LP(N) → σ*(Si–N) donation amounts to 17.8 kcal mol⁻¹ while the LP(N) → σ*(Si–C) hyperconjugation is only 11.2 kcal mol⁻¹ (Table S3, ESI†).

In summary, we have successfully synthesized the amidilanesilane trithiol RSi(SH)₃ (5) through protonation of its precursor [RSi(Si[THF])₃]₁₂ (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 LP(N) → σ*(Si–N) and LP(S) → σ*(Si–S) donations remarkably contribute to the stabilization of the Si(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.

Notes and references