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

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An interesting aminosilanetrithiol RSi(SH)$_3$ (R = N(SiMe$_2$)-2,6-iPr$_2$C$_6$H$_3$) has been prepared by the reaction of lithium aminosilanetrithiolate (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(COH)$_3$)$_3$ has been obtained by the reaction of sulfur with LiBE$_3$H, the reaction proceeded and several products were formed depending on the amount of Li$_2$S and the reaction conditions. As illustrated in Scheme 1, the reaction of 1 with 5.3 equivalents of Li$_2$Si(THF)$_3$ was carried out at 25 °C and stirred for 10 days, affording [RSi(SiLi(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 RSi(Li(THF))$_3$R$_2$ and RSi(SiLi(THF))$_3$Li. 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$_2$S. 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(Si$_2$Si)$_3$ 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$_3$ restricted temperature, long reaction time, and excess of Li$_2$S is important to the successful and high yield production of 2. 

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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, 13C and 29Si NMR spectra in solution, indicating that all the R groups in 2 are equivalent. The CHMe2 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 29Si NMR spectra of 2 display the respective resonances at 3.12 (SiMe3) and −4.2 ppm (SiS). The X-ray single-crystal structural analysis of 2 (Fig. 1) reveals that two Si(SiMe3)4 are assembled into a metal cage cluster which is comparable to those of the organosilanetriol-derived metallosiloxanes formed.3b–d The rhomboid-based dodecadedral Si2S6Li6 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 SiLi3 four-membered ring forms the base of the pyramid. Similar structures containing Si4N6Li6,15 Si2P6Li6,16 and Ge2As6Li6 frameworks have been reported.17

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 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 Si–SiMe3–N distance (1.712 Å) is computed to be 0.020 Å longer than the experimental value while the SiS bonds 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 ± 0.01; Si–C, 1.86 ± 0.01; Si–SH, 1.76 ± 0.01; Si–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)–2.110(7) Å; S–H, 1.31–1.34(3) Å; Si–Si–S, 94(4)–109(2)°) comparable to those found in Tbt(Mes)Si(SH)2, Tbt(Mes)Si(OH)SH,8 and LSi[Ni(CO)3]SH3 as well as in the predicted [Si(SiMe3)4]2+.

![Fig. 1 X-ray crystal structure of 2 with H atoms omitted for clarity.](image-url)
Since the NMR measurements were carried out in solution (CDCl₃), we optimized the geometry of 5 using the PCM (Polarized Continuum Model) method in which the effect by solvent was considered. Therefore, the geometry of 5 optimized at the PCM(CHCl₃)/M06-2X/def2-TZVPP level 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)₂ 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 moieties are at δ 0.35 and 11.25 ppm, respectively. These data generally fit to the experimental and the other related computational data. 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) analysis 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 from the sulfur (LP(S)) to the anti-bonding orbital σ*(Si–S) donation amounts to 17.8 kcal mol⁻¹ (Table S3, ESF). Furthermore, application of the second-order perturbation theory included in the NBO method. The LP(N) → σ*(Si–S) 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, ESF). The computed associated energies (ΔE[2]) are 13.54, 12.81 and 11.67 kcal mol⁻¹ for each of the LP(S) → σ*(Si–S) interactions.

In summary, we have successfully synthesized the amino-silanetriithoxy silsesquioxane (3) through protonation of its precursor [RSi(Si[TfH])₂]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 LP(N) → σ*(Si–S) and LP(S) → σ*(Si–S) donations remarkably contribute to the stabilization of the Si(Sh)₂ fragment. Compound 5 shows a structure containing three SiH groups attached to one element. The reactivity studies of 5 are now in progress. 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
13 We have tried H₂S in the liquid form at ca. 100 °C and allowed it to slowly warm to room temperature in the course of the reaction. We have also tested the group tolerance in the synthesises of compounds 2 and 5. Related results are shown in our recent patent which is still under authorization (CN10222598; Patent Application No. CN20111159112010050). However, compound 5 is selected as a typical example in this manuscript for profound experimental and theoretical studies.
17 We tried HCl or HClN₂ as the proton source. As a result, the chlorination happened and ionic (RCl₂SiS)₃⁻ was isolated.
23 Currently, we have obtained some preliminary results by isolating Ag₄ clusters of composition [R(THF)₅Si(THF)]₆ and [R(THF)₅Si(THF)]₆[Ag₂Me], which indicate a monofunctional 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 ESF.