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Aminosilanetrithiol RSi(SH)₃: An Experimental and Quantum-Chemical Study

Yan Li, Hongping Zhu, Diego M. Andrade, Gernot Frenking, Herbert W. Roesky

An interesting aminosilanetrithiol RSi(SH)₃ (R = N(SiMe₃)-2,6-iPr₂C₆H₃) has been prepared by the reaction of lithium aminosilanethiolate [RSi(SiLi(THF))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 (HC(OH)) and its sulfur congener (HC(SH)) are hypothetical molecules. Aqueous formic acid possibly contains HCOH which is 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, aryloxy, 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 (RSi(SH)) and diorganosilanediithiols (RSi(SH)₂) can be obtained by a variety of methods including alcoholysis of SiS₂, protonation of potassium silanethiolate, insertion of sulfur into triorganosilane, treatment of silylsulfide with hydrogen halide, and LiAlH₄ reduction of a silane polysulfide. More recently, a transition metal-trapped silylenylthiol LSi[Ni(CO)₃]SH (L = HC[MeCN-2,6-iPr₂C₆H₃]) has been achieved by 1,4-addition of H₂S to L'Si[Ni(CO)₃] (L' = HC[MeCN-2,6-iPr₂C₆H₃][C(THF)N-2,6-iPr₂C₆H₃]). In comparison with the preparation of the organosilanols, the synthesis of the organosilanethiols appears to be more complex. The approach to organosilanethiol by reacting the R'SiCl₃ (R' = Me₂PrC or Me) precursor with Li₂S³ or H₂S/NEt₃ in the presence of MeCl₂/SiSiCl₃/McCl¹¹ was not successful, and instead the silylsulfide clusters ((Me₅Si)₃Sₗ (and (Me₅Si)₂Sₕ) 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.

Scheme 1. Reaction of 1 with freshly prepared Li₂S under different reaction conditions to produce compounds 2-4.

The 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 RSiCl₃ (1, R = N(SiMe₃)-2,6-iPr₂C₆H₃) in the presence of amine as the HCl-acceptor, we used H₂S instead of H₂O. The experiments were carried out with different amines (NEt₃, 2,6-iPr₂C₆H₃NH₂, or pyridine) at various temperatures. No reaction was observed.

Subsequently, we employed 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 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(SiLi(THF)₂)]₂ (2) as colorless...
crystals in high yield (85%). However, changing the temperature, time, and ratio of the precursors the reaction only resulted in products RSiCl3(SiLi(THF))2 (3) and RSi(SiLi(THF))2(μ-Si(SH))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-S)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 literature, it is worth to note 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 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 δ 2.12 (SiMe3) and 4.2 ppm (SiS). The X-ray single-crystal structural analysis of 2 (Fig. 1) reveals that two Si(SLi)6 are assembled into a metal cage cluster which is comparable to those of the organosilanelanet-derivied metallosiloxanes formed. The rhomboïd-based dodecahedral Si3S6 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 SiLi4 four-membered ring forms the base of the pyramid. Similar structures containing Si3N6Li6, Si3P6Li8, and Ge3As6Li8 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) 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 ESI.

Compound 2 is a potential precursor for preparing aminosilanetriol. 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 CF3COOH, C6H5COOH, or p-MeC6H4SO3H 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 1H NMR spectrum of 5 clearly shows the SH proton resonance at δ 1.18 ppm, which is comparable to those found in Tbt(Mes)Si(OH)SH and Tbt(Mes)Si(OH)SH (6.87-1.87 ppm). The 29Si resonance (2.7 ppm) is remarkably lowfield shifted even to positive value in contrast to those of the SiO ones of the organosilaneanetrols (~40 to -90 ppm). A strong SH absorption band is observed at ν 2543 cm⁻1 in the IR spectrum.

The structural analysis unambiguously reveals 5 a monomeric molecule (Scheme 2). However, the refinements indicate a severe disorder for the N-bonded SiMe3 and Si(SH)2 groups which are pseudo-symmetrically arranged along the N-Caxial axis, although the Me and SH groups show different appearance (see Figure S4 in 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–MeC6H4N, 1.76 ± 0.01; Si–Si(NC6H4), 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, 2.10(1)-2.11(0) Å; S–H, 1.31-1.34(3) Å; Si–Si–S–H, 94(4)-109(2)°) comparable to those found in Tbt(Mes)Si(SH)3, Tbt(Mes)Si(OH)SH, and LSi[Ni(CO)3]SH as well as in the predicted [Si(SH)3]3⁻.

To further understand the bonding matrix of compound 5, we have 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-TZVP level, the general structure (Figure S6 in ESI) calculated is basically in agreement with the results by the X-ray structural analysis (Figure S4 in ESI). The Si8S8Si3N–N distance (1.712 Å) is computed to be ca. 0.020 Å longer than the experimental value while the Si8S4N–N one (1.774 Å) 0.014 Å shorter. Both the experimental and theoretical data are significantly shorter than the Si–N standard value (1.87 Å). 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 29Si NMR spectroscopic data by means of DFT-GIAO calculations. 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 an effect by solvent was considered. Therefore, the geometry of 5 optimized at the PCM(CHCl3)-M06-2X/def2-TZVP level is only slightly different from the one at the M06-2X/def2-TZVP20. 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 experimental19 and the other related computational data. Furthermore, the computed IR spectrum
exhibits a band for the SH groups at ν\textsuperscript{31} = 2753 cm\textsuperscript{-1}, which is a little higher than the experimental value.

A natural bond orbital (NBO) analysis\textsuperscript{24} 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 negative charge (-1.38 e) in a large extent while the silicon atoms have strong positive charges, namely, +1.91 e (for SiMe\textsubscript{3}) and +1.46 e (for Si(SH)). The Wiberg bond order values P for Si\textsubscript{2}S\textsubscript{2}N and Si\textsubscript{2}S\textsubscript{2}Ag\textsubscript{2}N bonds have been calculated at different levels of theory (Table S5). The data point out that the former (P = 0.61-0.63) has a higher bond order than the later (P = 0.56-0.58). The former one can be explained by hyperconjugation of the lone pair orbital of the nitrogen, which is calculated by using second-order perturbation theory included in the NBO method. The LP(N)→σ*(Si-S) donation amounts to 17.8 kcal/mol while the LP(S)→σ*(Si-C) hyperconjugation is only 11.2 kcal/mol (Table S3 in ESI). Furthermore, application of the second-order perturbation theory revealed delocalization of three stabilizing two-electrons from the sulfur (LP(S)) to the anti-bonding orbital σ*(Si-S), giving hints of a high conjugation of the Si(SH)\textsubscript{2} fragment. The computed associated energies (∆E) are 13.54, 12.81 and 11.67 kcal/mol for each of the LP(S)→σ*(Si-S) interaction.

In summary, we have successfully synthesized the compound was determined. The synthesis of these two compounds and crystallographic data of \textsuperscript{(AgMes)}\textsubscript{2} S 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 syntheses of compounds 2 and 5. Related results are shown in our recent patent which is still under authorization (CN102225289; Patent Application No. CN2011115911 20110505). However, compound 5 is selected as a typical example in this manuscript for profound experimental and theoretical studies.


We tried HCl or HCl\textsubscript{2}N\textsubscript{3} as the proton source. As a result, the chlorination happened and ion (RCl\textsubscript{3})\textsuperscript{+} (HNEt\textsubscript{3})\textsuperscript{-} was isolated.


