A Disilane Containing Two Heptacoordinate Silicon Atoms and Dithiocarboxylate Ligands**

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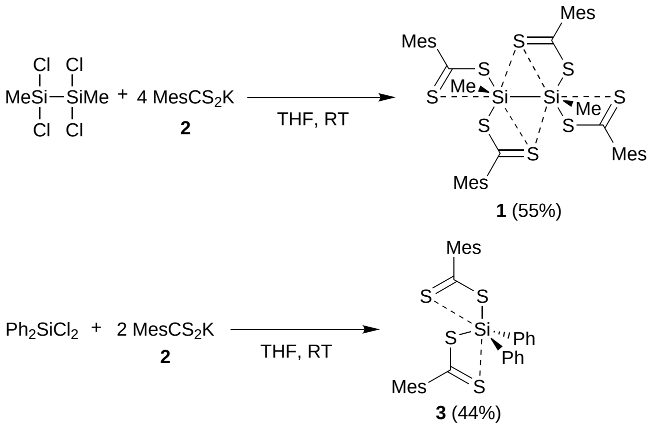
Organosilicon compounds with high coordination numbers have been extensively studied because of their interesting structural features and synthetic utility.[1] Disilanes that contain exclusively hypervalent silicon atoms are of current interest as components of high-coordination-number polysilanes, which are expected to show unique electronic and optical properties.[2] In spite of theoretical predictions that Si–Si bonds are not good candidates for hypercoordination, a few examples of pentacoordinate silylsilicates have been reported, as in the cases of disilanes with pentacoordinate or hexacoordinate silicon atom(s) due to intramolecular coordination of oxygen or nitrogen atoms.[3, 4] However, there have been no reports on disilanes with hepta- or octacoordinate silicon atoms.[5] Compounds of Group 14 elements containing dithiocarboxylate ligands (RCS_2^-) are known to exhibit intramolecular interaction between the central atom (Ge, Sn, and Pb) and the thiocarbonyl sulfur atom.[6] Although such an intramolecular coordination is expected for silicon analogues, few examples of $RCS_2SiR'_3$ have been reported, and no X-ray structures are available.[6a,c, 7] Here we report on a monosilane and a disilane with two dithiocarboxylate ligands on each Si atom; the latter is the first structurally characterized heptacoordinate disilane.

Compound **1** was synthesized in 55% yield by the reaction of 1,1,2,2-tetrachloro-1,2-dimethyldisilane with 4.4 equivalents of potassium 2,4,6-trimethyldithiobenzoate (**2**, Scheme 1), which was prepared from the corresponding arenecarbodithioic acid and potassium hydride.[8] Compound **3** was similarly synthesized from dichlorodiphenylsilane and 2.1 equivalents of **2** in 44% yield (Scheme 1). Compounds **1** and **3** are thermally quite stable, but highly sensitive to moisture. The alcoholysis of **1** and **3** with absolute ethanol in C_6D_6 at room temperature occurred immediately and quantitatively to give $(EtO)_2MeSiSiMe(OEt)_2$ and $(EtO)_2SiPh_2$, respectively, together with 2,4,6-trimethyldithiobenzoic acid.



Scheme 1. Synthesis of **1** and **3**. Mes = 2,4,6-trimethylphenyl.

An X-ray crystallographic analysis was performed on **3** to clarify whether the thiocarbonyl groups interact with the silicon atom.[9] The unit cell contains two independent molecules of **3** that are very similar to each other. The ORTEP plot of one molecule is shown in Figure 1. Compound **3** has a slightly distorted tetrahedral structure, as indicated by the bond angles (99.3(3)–116.5(3)°) around the silicon atom. Both thiocarbonyl groups of the $MesCS_2$ ligands are directed towards the central silicon atom, as reported previously for heavier analogues.[6] Thiocarbonyl sulfur atoms S2 and S4 are located on the opposite side to S3 and C1, respectively, in contrast to the situation of the tin compound $(4\text{-}MeC_6H_4CS_2)_2Sn_2Ph$.[6d] The intramolecular distances between the silicon and thiocarbonyl sulfur atoms S2 and S4 are 3.315(3) and 3.341(3) Å, respectively, which are considerably shorter than the sum of the van der Waals radii (3.90 Å), although they are much longer than the sum of the corresponding covalent-bond radii (2.22 Å).[10] The ratio of M···S intramolecular distances and the sum of the corresponding van der Waals radii (14 or 15%) is similar to those of $(4\text{-}CH_3C_6H_4CS_2)MPh_3$ (M = Ge, 11%; M = Sn, 19%; and M =

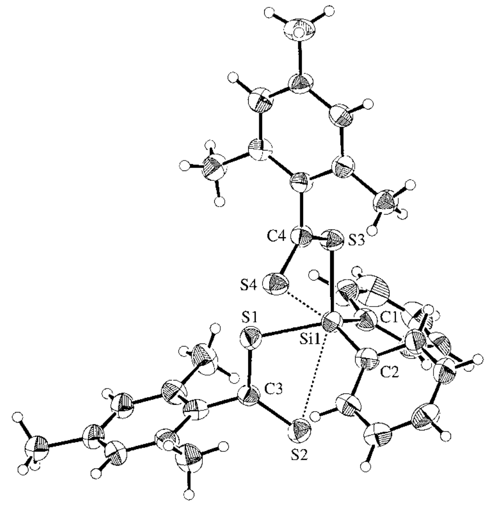


Figure 1. ORTEP plot of **3** (30% probability thermal ellipsoids for all non-hydrogen atoms). Selected bond lengths [Å], interatomic distances [Å], and bond angles [°]: Si1-S1 2.165(3), Si1-S3 2.183(3), Si1-C1 1.842(9), Si1-C2 1.841(10), C3-S1 1.743(8), C3-S2 1.646(9), C4-S3 1.745(9), C4-S4 1.630(9), Si1···S2 3.315(3), Si1···S4 3.341(3); S1-Si1-S3 102.17(12), S1-Si1-C1 112.0(3), S1-Si1-C2 116.5(3), S3-Si1-C1 99.3(3), S3-Si1-C2 111.2(3), C1-Si1-C2 113.8(4), Si1-S1-C3 104.6(3), Si1-S3-C4 104.6(3).

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Pb, 12%).[6d] These structural features of **3** are indicative of intramolecular Si–S interactions and a neutral, hexacoordinate silicon atom. Such an interaction was also observed for silanyl monothioacetate.[11] The C–S bond length (1.743(8) and 1.745(9) Å) lies between the sums of the covalent radii for a C–S single (1.81 Å) and double bond (1.62 Å), while the C=S bond lengths (1.646(9) and 1.630(9) Å) are close to the value for a double bond. Two Si–S bond lengths (av 2.174 Å) and two Si–C bond lengths (av 1.842 Å) show almost no differences from those previously reported for $Me_2Si(SR)_2$.[12] This is the first X-ray analysis of an organosilicon compound bearing dithiocarboxylate ligands.

A similar coordination of thiocarbonyl sulfur atoms to the silicon atoms was also observed in the X-ray structure of $\mathbf{1}\cdot C_6H_6$ (Figure 2).[9] The four Si–S (2.184(3)–2.199(3) Å) and two Si–C bond lengths (1.856(9) and 1.862(9) Å) showed minor differences from those of **3**. The Si1–Si2 bond length (2.351(3) Å) is almost the same as those of $Me(RS)_2$-Si–SiMe(SR)$_2$ (2.3481(11)–2.3642(11) Å).[12] In the case of Si1, the thiocarbonyl sulfur atoms S4 and S2 are located opposite to Si2 (3.461(3) Å) and S3 (3.049(3) Å), respectively. The sulfur atoms of the other two thiocarbonyl groups have a similar arrangement with respect to the Si2 atom. Thiocarbonyl sulfur atoms S2 and S6 are both located in the vicinity of both silicon atoms, while the other thiocarbonyl sulfur atoms are close (3.461(3), 3.478(3) Å) to only one silicon atom.[13] Since the interatomic Si⋯S distances are within the sum of the van der Waals radii, disilane **1** clearly contains two heptacoordinate silicon atoms with four covalent bonds and three weak Si⋯S intramolecular interactions. On the other hand, the bond angles (97.5(1)–117.8(3)°) around the silicon atoms indicate retention of the basic tetrahedral structure. Disilane **1** adopts a nearly eclipsed conformation along the Si–Si bond axis according to the corresponding torsion angles (12.4(4)–19.9(2)°). Such a conformation facilitates the coordination of S2 and S6 to the two silicon atoms, which thus avoid steric repulsion of each other. If the silicon atoms adopted a staggered conformation, the thiocarbonyl sulfur atom which is coordinated to two silicon atoms would impinge upon another sulfur atom. This is the first example of a heptacoordinate disilane in which two silicon atoms with tricapped tetrahedral structures are directly connected to each other. The intramolecular Si⋯S interactions of **1** and **3**, which are weak, as indicated by the interatomic distances, are responsible for the heptacoordinate state of the silicon atoms of **1**, in contrast to previously reported disilanes with high coordination numbers.[4]

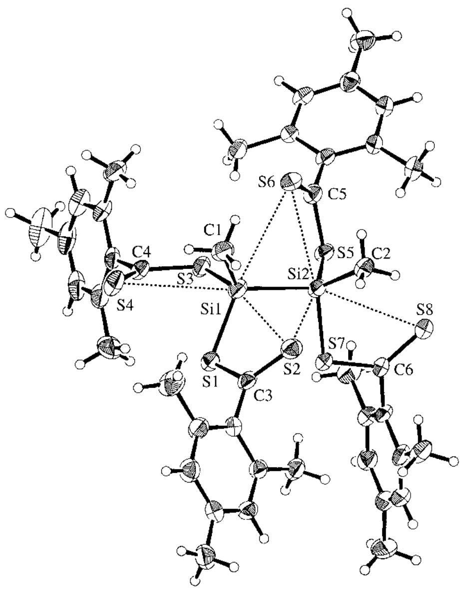

Figure 2. ORTEP plot of $\mathbf{1}\cdot C_6H_6$ (30% probability thermal ellipsoids for all non-hydrogen atoms). Benzene molecules are omitted for clarity. Selected bond lengths [Å], interatomic distances [Å], bond angles [°], and torsion angles [°]: Si1-Si2 2.351(3), Si1-C1 1.856(9), Si2-C2 1.862(9), Si1-S1 2.193(3), Si1-S3 2.184(3), Si2-S5 2.199(3), Si2-S7 2.184(3), C3-S1 1.757(8), C3-S2 1.620(8), C4-S3 1.759(8), C4-S4 1.616(9), C5-S5 1.745(8), C5-S6 1.648(9), C6-S7 1.761(8), C6-S8 1.624(9), Si1⋯S2 3.049(3), Si1⋯S4 3.461(3), Si1⋯S6 3.438(4), Si2⋯S2 3.356(4), Si2⋯S6 3.076(3), Si2⋯S8 3.478(3); S1-Si1-S3 99.8(1), S1-Si1-C1 112.3(3), S1-Si1-Si2 111.6(1), S3-Si1-C1 113.6(3), S3-Si1-Si2 99.7(1), C1-Si1-Si2 117.8(3), S5-Si2-S7 97.5(1), S5-Si2-C2 111.1(4), S5-Si2-Si1 112.1(1), S7-Si2-C2 115.8(3), S7-Si2-Si1 100.4(1), C2-Si2-Si1 117.8(3), Si1-S1-C3 97.9(3), Si1-S3-C4 106.7(3), Si2-S5-C5 99.3(3), Si2-S7-C6 107.3(3), S1-Si1-Si2-S7 14.5(4), S3-Si1-Si2-S5 12.4(4), C1-Si1-Si2-C2 19.9(2).

The high coordination number of the silicon atoms in **1** and **3** is firstly attributable to the interaction of the lone pair on the thiocarbonyl sulfur atom with the corresponding σ* orbitals of Si–S, Si–C, or Si–Si bonds on their opposite sides, as observed in other compounds of Group 14 elements with dithiocarboxylate ligands.[6e] Secondly, their lone pairs may additionally interact with the $\sigma^*_{\text{Si-S}}$ orbitals of the same dithiocarboxylate ligand.[14] The combination of these interactions could be responsible for the widely ranging interatomic Si⋯S distances in **1**.

In the ^{1}H and ^{13}C NMR spectra of **1** and **3**, the signals for all thiocarbonyl carbon atoms, all mesityl groups, two methyl groups on the silicon atoms of **1**, and two phenyl groups of **3** were equivalent. The chemical shifts of the carbon atoms of thiocarbonyl groups were similar to those of other compounds of Group 14 elements with dithiocarboxylate ligands.[6e] In the ^{29}Si NMR spectra, signals of **1** ($\delta_{Si} = -11.9$) and **3** ($\delta_{Si} = -10.1$) were observed in a similar region to that of $MesCS_2$-$SiPh_3$ ($\delta_{Si} = -6.4$)[15] and were shifted upfield relative to those of $Ph_2Si(S\textit{n}Bu)_2$ ($\delta_{Si} = 10.1$) and $Me(RS)_2SiSiMe(SR)_2$ ($\delta_{Si} = 9.7$ for R = Ph and $\delta_{Si} = 0.1$ for R = *t*Bu).[16] Some of the intramolecular Si–S interactions appear to be maintained in solution, judging from the upfield shifts. The chemical shifts are in low-field regions for hexacoordinate and heptacoordinate silicon atoms, and this indicates that the coordination of the sulfur atoms to the silicon atom is weak. In the UV/Vis spectra, the n–π* transition of **1** was observed 23 nm to shorter wavelength than that of **3**. This blue shift is most likely to originate in the stabilization of the ground state of **1** by the larger number of orbital interactions between the lone pairs of thiocarbonyl sulfur atoms and σ* orbitals of Si–C, Si–S, or Si–Si bonds, which lie at the relatively low-energy levels of the silicon atoms.

In summary, we have synthesized monosilane **3** and disilane **1**, each of which bears two [2,4,6-trimethyl(thiobenzoyl)]thio ligands on each silicon atom, and determined their structures. Compound **3** has a hexacoordinate structure with weak intramolecular interactions between the silicon atom and the sulfur atoms of thiocarbonyl groups. X-ray analysis of disilane **1** revealed the direct connection between of two heptacoordinate silicon atoms. Heptacoordination of the silicon atoms in **1** is achieved by an additional intramolecular coordination of one thiocarbonyl sulfur atom to the silicon atom to which its [2,4,6-trimethyl(thiobenzoyl)]thio group is not attached. These results not only showed an interesting structural similarity between compounds of silicon and those of other Group 14 elements, but also suggested the possibility of synthesizing polysilanes with high coordination numbers.

Experimental Section

1: 1,1,2,2-Tetrachloro-1,2-dimethyldisilane (0.038 mL, 0.21 mmol) was added to a solution of **2** (0.216 g, 0.925 mmol) in THF (4 mL) at room temperature. After stirring for 30 min, the solvent was evaporated under reduced pressure. After insoluble materials were removed, the residue was recrystallized from hexane and benzene to give red crystals of **1** (0.101 g, 55 %). M.p. 209–210 °C (decomp); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 1.61$ (s, 6H), 2.08 (s, 12H), 2.43 (s, 24H), 6.64 (s, 8H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 3.18$ (q), 19.69 (q), 20.90 (q), 128.97 (d), 132.10 (s), 138.00 (s), 146.68 (s), 242.38 (s, C=S); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -11.90$ (s); UV/Vis (hexane): λ_{max} (lg ε) = 312 (4.5), 496 nm (2.3); IR (KBr): $\tilde{\nu} = 1255$ cm^{-1} (br, C=S); Elemental analysis (%) calcd for $C_{42}H_{50}S_8Si_2$: C 58.15, H 5.81; found: C 57.38, H 6.15.

3: Dichlorodiphenylsilane (0.095 mL, 0.45 mmol) was added to a solution of **2** (0.225 g, 0.960 mmol) in THF (4 mL) at room temperature. After stirring for 30 min, the solvent was evaporated under reduced pressure. After insoluble materials were removed, the residue was recrystallized from hexane to give red crystals of **3** (0.113 g, 44 %). M.p. 180–184 °C (decomp); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 2.05$ (s, 6H), 2.29 (s, 12H), 6.61 (s, 4H), 7.10–7.18 (m, 6H), 8.14–8.15 (m, 4H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 19.27$ (q), 20.90 (q), 128.83 (d), 129.46 (s), 131.19 (d), 131.75 (s), 135.18 (d), 136.48 (d), 137.68 (s), 147.29 (s), 238.42 (s, C=S); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -10.14$ (s); UV/Vis (hexane): λ_{max} (lg ε) = 318 (4.4), 519 nm (2.0); IR (KBr) $\tilde{\nu} = 1261$ (C=S), 1241 cm^{-1} (C=S); Elemental analysis (%) calcd for $C_{32}H_{34}S_4Si$: C 67.08, H 5.63; found: C 66.84, H 5.85.

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[9] Crystal data for **3**: $C_{32}H_{32}S_4Si$, $M_r = 572.93$, orthorhombic, space group $Pca2_1$, $Z = 8$, $a = 21.050(2)$, $b = 8.9930(6)$, $c = 32.988(2)$ Å, $V = 6244.7(6)$ Å^3, $\rho_{calcd} = 1.22$ g cm^{-3}. X-ray diffraction data were collected on a MAC Science DIP-2030 imaging-plate area detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at −100 °C, and the structure was solved by direct methods (SIR92). The final cycle of full-matrix least-squares refinement was based on 4516 observed reflections ($I > 3\sigma(I)$) and 731 variable parameters and converged to $R = 0.060$ and $R_w = 0.096$. Crystal data for $\mathbf{1} \cdot C_6H_6$: $C_{48}H_{56}S_8Si_2$, $M_r = 945.62$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 11.269(2)$, $b = 13.577(3)$, $c = 18.297(4)$ Å, $\alpha = 71.86(1)$, $\beta = 78.80(1)$, $\gamma = 73.71(1)^\circ$, $V = 2535.8(1)$ Å^3, $\rho_{calcd} = 1.24$ g cm^{-3}. X-ray diffraction data were collected on a MAC Science DIP-2030 imaging-plate area detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at −100 °C, and the structure was solved by direct methods (SIR92). The final cycle of full-matrix least-squares refinement was based on 3973 observed reflections ($I > 3\sigma(I)$) and 579 variable parameters and converged to $R = 0.074$ and $R_w = 0.113$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-162119 (**3**) and CCDC-162120 ($\mathbf{1} \cdot C_6H_6$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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