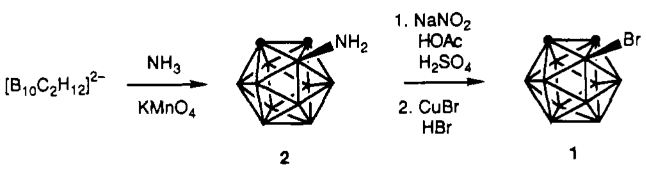
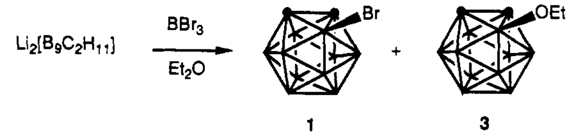


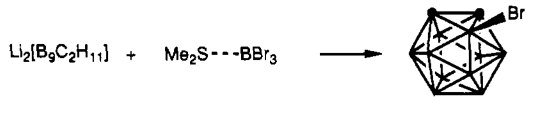
The easiest current route to **1** is that of Roscoe, Kongpricha, and Papetti,[4] which involves the treatment of $Li_2[B_9C_2H_{11}]$ with boron tribromide. Two bromides are displaced, and the residual B–Br is incorporated into the icosahedral cage at the 3-position. Although the reaction as described is not difficult to carry out, the yield reported is only 26% and we have found that complications are introduced by the necessity of separating an unreported side product formed in approximately the same yield as **1**. We have identified this compound as 3-ethoxy-*o*-carborane (3).[5]



A mechanistic analysis of the Roscoe procedure points out a probable source of 3 and suggests an effective modification. Boron tribromide is a well-known reagent used for ether cleavage reactions.[6] Complex formation is followed by displacement by bromide with formation of ethoxydibromoborane, doubtless the active ingredient in the formation of 3 in the Roscoe procedure.

$$Et_2O + BBr_3 \longrightarrow EtOBBr_2 \xrightarrow{Li_2[B_9C_2H_{11}]} 3$$

In order to avoid this simple, but seriously offending side reaction, we need only thwart the ether cleavage reaction. The boron tribomide–methyl sulfide complex is commercially available[7] and serves to convert $Li_2[B_9C_2H_{11}]$ into **1** without complicating side products. Pure material can be obtained in >65% yield after recrystallization from chloroform/hexanes.



1, 65.4%

Experimental Section

3-Bromo-*o*-carborane (1). $[Me_3NH][B_9C_2H_{12}]$[8] (1.25 g, 6.5 mmol) was placed in 30 mL of methyl sulfide in a 250-mL, three-necked flask equipped with a magnetic stirrer, reflux condenser, and a gas inlet and outlet. The system was flushed slowly with argon while the reaction was in progress. A solution of 2.5 M *n*-butyllithium in hexane (5.2 mL, 13 mmol) was slowly added with a syringe to the mixture with stirring at room temperature. After the addition was completed, the reaction mixture was stirred at room temperature for an additional 2 h and then heated to reflux for 4 h. After the reaction mixture cooled to room temperature, the boron tribromide–methyl sulfide complex (2.5 g, 7.9 mmol) was added slowly, with vigorous stirring. The stirring was continued for another 2 h after the addition was completed. The reaction mixture was then hydrolyzed with 2 mL of water to remove the excess boron tribromide. The organic layer was separated out and then evaporated to dryness under vacuum. The resulting solid was purified by recrystallization from chloroform/hexanes to give 3-bromo-*o*-carborane (950 mg, 65.4% yield). Mp: 118–120 °C (lit. 118.5–119,[3] 121–122 °C[4]). ^1H NMR (δ, $CDCl_3$): 3.82 (s, 2 H), 3.55–1.12 (m, 9 H). MS [*m*/*e* (assignment, % relative intensity)]: 225 (M + 2, 26), 224 (M + 1, 52), 223 (M, 83), 222 (M − 1, 100), 221 (M − 2, 98), 220 (M − 3, 75), 199 (M − 4, 52), 142 (12).

3-Ethoxy-*o*-carborane (3). This material was produced by using the procedure of Roscoe et al.[4] Mp: 40–41 °C (lit.[5] 38 °C). ^1H NMR (δ, $CDCl_3$): 3.94 (q, 2 H), 3.53 (s, 2 H), 3.45–1.32 (m, 9 H), 1.27 (t, 3 H). MS [*m*/*e* (assignment, % relative intensity)]: 190 (M + 2, 5), 189 (M + 1, 13), 188 (M, 16), 187 (M − 1, 13), 173 (M − 15, 100), 159 (M − 29, 18).

Registry No. 1, 22258-25-9; **3**, 52138-59-7; $[Me_3NH][B_9C_2H_{12}]$, 12543-22-5; $Li_2[B_9C_2H_{11}]$, 62601-97-2.

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Models for Structural Environments in Silicon Chalcogenide Glasses. Synthesis, Characterization, and Single-Crystal X-ray Structures of $Si(SC_6H_5)_4$ and $Si(SeC_6H_5)_4$

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Introduction

Non-oxide chalcogenide glasses, which are formed by the sulfides, selenides, and tellurides of many main-group elements are important materials with promising applications in infrared optics and semiconductor technology. The development of materials with improved properties for device applications remains an important goal in this area of study, which requires a detailed structural description of the glassy state and its relationship to the physicochemical properties. These objectives necessitate the use of suitable techniques, such as solid-state NMR, which can probe the short-range order present in these systems.

To appropriately interpret NMR spectra of glasses, corresponding benchmark data on compounds with crystallographically well-characterized local environments are required. Therefore, in our continuing effort to understand the structural organization of silicon chalcogenide glasses, we report here the preparation, characterization, and single-crystal X-ray structures of two compounds with the anticipated $SiCh_{4/2}$ (Ch = S, Se) connectivity, namely $Si(SC_6H_5)_4$ and $Si(SeC_6H_5)_4$.

Experimental Section

Sample Preparation and Characterization. Chemicals. Thiophenol (Aldrich, 97%) was dried over P_2O_5 and then vacuum distilled. Benzene (Fisher) was dried over P_2O_5 and then distilled under N_2. Sodium (Fisher), phenylselenol (Alfa), silicon tetrachloride (Aldrich), and anhydrous ethyl ether (Fisher) were used without further purification. The synthetic procedures follow those published previously for these compounds.[1,2]

Preparation of $Si(SC_6H_5)_4$. Excess thiophenol (70 mL, 684 mmol) was added to 2 g (87.0 mmol) of sodium under N_2. This, at times vigorous, reaction was allowed to continue overnight at room temperature with intermittent stirring to yield a suspension of white $NaSC_6H_5$ in thiophenol. To this suspension was slowly added silicon tetrachloride (0.90 mL, 7.9 mmol) with swirling. After the initial reaction subsided, the mixture was heated at 90 °C for 15 min. NaCl and excess $NaSC_6H_5$ were filtered off, and the crude $Si(SC_6H_5)_4$ was then isolated from the solution. Recrystallization of $Si(SC_6H_5)_4$ from an anhydrous ethyl ether–thiophenol solution (30:1) by the slow evaporation of ether resulted in colorless crystals, yield 1.24 g (34%). Mp: 115.0 °C (lit.[2] mp: 114.5 °C). Mass spectrum: parent peak at 464 g/mol.

Preparation of $Si(SeC_6H_5)_4$. A suspension of white $NaSeC_6H_5$ was synthesized by the reaction of sodium (0.698 g, 30.4 mmol) and benzeneselenol (5 g, 32 mmol) in 50 mL of benzene. To this suspension was added silicon tetrachloride (0.670 mL, 5.85 mmol) at room temperature. After 1 week at room temperature, the mixture was warmed to 45 °C for 15 min and subsequently cooled. Excess $NaSeC_6H_5$ and NaCl were filtered out and the crude $Si(SeC_6H_5)_4$ was isolated. The product was recrystallized in an ethyl ether–benzeneselenol solution (30:1) and then washed with a minimum of ethyl ether to give colorless crystals, yield

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(1) Backer, H. J.; Hurenkamp, J. B. G. *Recl. Trav. Chim. Pays-Bas* **1942**, *61*, 802.
(2) Backer, H. J.; Stienstra, F. *Recl. Trav. Chim. Pays-Bas* **1933**, *52*, 912.

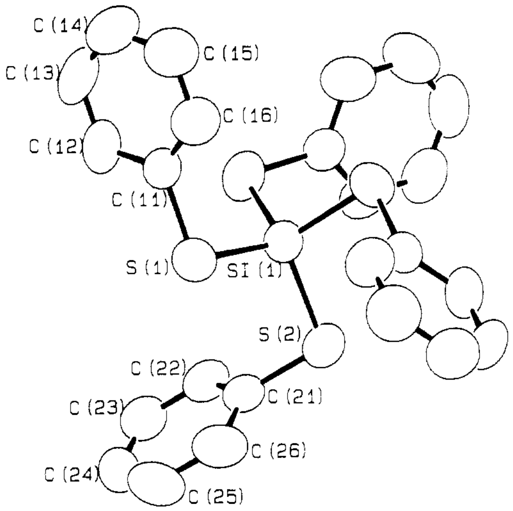

Figure 1. Molecular structure of $Si(SC_6H_5)_4$. Atoms comprising the asymmetric unit have been labeled and hydrogen atoms omitted for clarity. ORTEP drawing shows 50% probability ellipsoids.

1.11 g (29%). Mp: 138.0 °C (lit.[1] mp: 136.5 °C). Mass spectrum: parent peak cluster at 649.7, 651.7, 653.7, and 655.7 g/mol.

NMR Studies. NMR experiments were carried out on a General Electric GN-300 instrument. Solution-state ^{29}Si NMR spectra were obtained in a multinuclear probe with a 90° pulse length of 20 μs and a recycle delay 60 s, ^1H broad-band decoupling during acquisition. Solid-state ^{29}Si NMR spectra were obtained in the single-pulse mode (7 μs 90° pulse, 2 h recycle delay) by using a multinuclear broad-band MAS-NMR probe from Doty Scientific (spinning speed 3.5 kHz).

X-ray Crystallography. $Si(SeC_6H_5)_4$. A fragment of dimensions 0.8 × 0.6 × 0.3 mm, cut from a roughly hexagonal plate, was used in the X-ray diffraction study. Data were collected on a Huber four-circle diffractometer automated by Crystal Logic, Inc. utilizing graphite monochromatized Mo Kα radiation. A total of 2563 reflections (positive quadrant) were measured in the $\theta/2\theta$ scan mode to a maximum 2θ of 65° at a scan speed of 6°/min. Three standard reflections were measured after every 97 reflections and showed no evidence of crystal decomposition. The data were corrected for Lorentz and polarization effects,[3] and an analytical absorption correction was applied.[4] A total of 1357 reflections with $I > 3\sigma(I)$ were used in the structural analysis. Inspection of the intensity data revealed the systematic absences $0kl$, $k = 2n + 1$; $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$, consistent with the space groups *Pba*2 (No. 32) and *Pbam* (No. 55). Two $Si(SeC_6H_5)_4$ molecules can be accommodated in the volume of the unit cell; thus, the acentric space group *Pba*2, with half the molecule comprising the asymmetric unit, was chosen. The half Si atom and both unique chalcogen atoms were located utilizing the direct methods program SHELXS.[5] The carbon atoms were located by successive cycles of full-matrix, least-squares refinement and difference Fourier synthesis. In the final refinement,[6] the Si was constrained to lie on the 2-fold axis and its anisotropic thermal parameter was refined with the appropriate constraint. The positions and anisotropic thermal parameters of all other non-hydrogen atoms were refined. The positions of the phenyl hydrogen atoms were calculated (C–H bond length 1.0 Å) and they were included as fixed contributors with isotropic thermal parameters fixed to 5.0 Å^2. The refinement converged[7] at $R = 6.6$ and $R_w = 7.4$.

$Si(SC_6H_5)_4$. A hexagonal crystal of dimensions 0.1 mm × 0.1 mm × 0.1 mm was utilized. Data collection and analysis for this isomorphous crystal were analogous to that for the Se analogue with the following exceptions: a total of 951 reflections were collected at a scan rate of 4.5°/min to a maximum 2θ of 45°; an empirical absorption correction[8] was applied, and a total of 651 reflections with $I > 3\sigma(I)$ were used in the structural analysis. The non-hydrogen atom positions for the Se

Table I. Crystallographic Data for $Si(SeC_6H_5)_4$ and $Si(SC_6H_5)_4$

chem formula	$Si(SeC_6H_5)_4$	$Si(SC_6H_5)_4$
fw	652.4	464.8
ρ_{calc}, g cm^{-3}	1.76	1.29
a, Å	8.5636 (4)	8.6093 (5)
b, Å	17.120 (1)	17.006 (2)
c, Å	8.3900 (4)	8.1451 (6)
V, Å^3	1230	1192
space group (No.)	*Pba*2 (32)	*Pba*2 (32)
Z	2	2
λ, Å	0.71069	0.71069
T, °C	23	23
μ, cm^{-1}	59.6	4.40
transm coeff	0.092–0.194	0.78–1.00
R	6.6	3.6
R_w	7.4	4.3

Table II. Positional Parameters for $Si(ChC_6H_5)_4$

atom	x	y	z
	(a) Ch = Se		
Si(1)	0.0000	0.0000	0.3866
Se(1)	−0.0388 (1)	0.1114 (1)	0.5287 (6)
Se(2)	0.2213 (1)	0.0209 (1)	0.2435 (6)
C(11)	0.1696 (13)	0.1180 (5)	0.6153 (15)
C(12)	0.2780 (13)	0.1696 (7)	0.5542 (17)
C(13)	0.4266 (14)	0.1741 (8)	0.6207 (21)
C(14)	0.4628 (14)	0.1285 (10)	0.7488 (27)
C(15)	0.3553 (18)	0.0792 (10)	0.8143 (19)
C(16)	0.2067 (14)	0.0736 (8)	0.7528 (20)
C(21)	0.2497 (13)	−0.0842 (7)	0.1665 (16)
C(22)	0.1605 (14)	−0.1134 (7)	0.0448 (20)
C(23)	0.1849 (17)	−0.1883 (9)	−0.0114 (19)
C(24)	0.2948 (19)	−0.2357 (8)	0.0571 (28)
C(25)	0.3846 (20)	−0.2049 (10)	0.1827 (23)
C(26)	0.3633 (14)	−0.1311 (9)	0.2355 (18)
	(b) Ch = S		
Si(1)	0.0000	0.0000	0.3866
S(1)	−0.0289 (2)	0.1055 (1)	0.5239 (5)
S(2)	0.2075 (2)	0.0167 (1)	0.2502 (5)
C(11)	0.1620 (7)	0.1148 (3)	0.6119 (10)
C(12)	0.2650 (9)	0.1695 (4)	0.5448 (12)
C(13)	0.4125 (10)	0.1758 (5)	0.6149 (13)
C(14)	0.4522 (9)	0.1307 (6)	0.7483 (16)
C(15)	0.3492 (11)	0.0777 (5)	0.8126 (11)
C(16)	0.2047 (9)	0.0706 (4)	0.7459 (13)
C(21)	0.2408 (7)	−0.0800 (4)	0.1725 (10)
C(22)	0.1538 (8)	−0.1109 (4)	0.0473 (12)
C(23)	0.1811 (9)	−0.1856 (5)	−0.0111 (12)
C(24)	0.2984 (11)	−0.2302 (4)	0.0533 (17)
C(25)	0.3880 (10)	−0.2000 (6)	0.1779 (14)
C(26)	0.3615 (8)	−0.1241 (5)	0.2382 (12)

Table III. Solid-State ^{29}Si NMR Chemical Shifts of Silicon–Sulfur and Silicon–Selenium Compounds

compd	$\delta_{iso}(^{29}Si)/ppm^a$	ref
SiS_2	−21.1	9
$Na_4Si_4S_{10}$	2.9/0.7	9
Na_4SiS_4	8.6	9
Na_2SiS_3	3.2	9
$Si(SC_6H_5)_4$	25.5	*b*
$SiSe_2$	−92.6	*c*
$Si(SeC_6H_5)_4$	11.0	*b*

[a] ±0.1 ppm vs TMS. [b] This work. [c] To be published.

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(6) Scattering factors and corrections for anomalous dispersion were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England 1974; Vol. IV.

(7) All least-squares refinements computed the agreement factors R and R_w according to

$$R = \frac{\sum(||F_o| - |F_c||)}{\sum|F_o|}$$

$$R_w = \left[\frac{\sum(w(||F_o| - |F_c||)^2}{\sum(w|F_o|)^2}\right]^{1/2}$$

where F_o is the observed structure factor, F_c is the calculated structure factor, and $w = 1/\sigma(F_o)^2$.

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Table IV. Compilation of Published Si–S and Si–Se Bond Lengths and Si–S–C Bond Angles[a]

compd	d(Si–S)/Å	n_s	ref
SiS_2	2.133	4	10
$Si(S_2C_2H_4)_2$	2.117, 2.115	4	11
$Si_4S_6(SC_6H_5)_2(S^-)_2$	2.124, 2.114, 2.116, 2.128	4	
	2.135, 2.111, 2.120, 2.117	4	
	2.156, 2.159, 2.135, 2.024	4^b	
	2.130, 2.149, 2.149, 2.038	4^b	26
$Si(SC_6H_5)_3S^-$	2.162, 2.150, 2.160, 2.023	4^b	26
$Si(SC_6H_5)_4$	2.123, 2.129	4	*c*
$[(C_6H_5S)_3Si]_2$	2.139, 2.147, 2.133	3	26
$(CH_3Si)_4S_6$	2.133, 2.121, 2.132		
	2.130, 2.127, 2.131	3	12
$(HSi)_4S_6$	2.137, 2.133, 2.134	3	28
$[(CH_3)_2SiS]_2$	2.152	2	13
$[(t\text{-}C_4H_9O)_2SiS]_2$	2.131, 2.142	2	15
$[CH_3C_6H_5SiS]_3$	2.142, 2.151, 2.126		
	2.153, 2.139, 2.147	2	16
$[(t\text{-}C_4H_9O)_3Si]_2S$	2.152, 2.150	1	14
$[RN(CH_3)_2Si]_2S$	2.151, 2.146	1	17
$[R_2CH_3Si]_2S$	2.156, 2.137	1	18
$(C_6H_5)_3SiSC_6H_5$	2.156	1	19
$(C_6H_5)_3SiSCH_3$	2.138	1	21
$[(C_6H_5)_3Si]_2S$	2.153, 2.150	1	22
$(CH_3)_{10}Si_6S$	2.169	1	20
$(H_3Si)_2S$	2.142, 2.141	1	27
$(CH_3)_3SiSR$	2.166, 2.159, 2.157, 2.155	1	23
$(CH_3)_3SiSR'$	2.161	1	24
$(CH_3)_3SiSR''$	2.186, 2.185	1	25
$SiSe_2$	2.275	4	10
$Si(SeC_6H_5)_4$	2.274, 2.272	4	*c*
$(H_3Si)_2Se$	2.253, 2.291	1	27

compound	α(Si–X–C)/deg	ref
$Si(SC_6H_5)_4$	100.17, 101.39	*c*
$Si(SeC_6H_5)_4$	96.39, 97.78	*c*
$Si(S_2C_2H_4)_2$	96.8, 97.2	11
$(C_6H_5)_3SiSC_6H_5$	99.5	19
$(C_6H_5)_3SiSCH_3$	102.6	21
$(CH_3)_3SiSR$	107.2, 109.0, 109.0, 107.4	23
$(CH_3)_3SiSR'$	106.5	24
$(CH_3)_3SiSR''$	111.7, 110.4	25

[a] Emphasis is on the Si connectivity, and formulas have been abbreviated in some cases. For detailed formulas, see the references. [b] Si atom bonded to a charged S^- species. [c] This work.

analogue were used as a starting model in the refinement of this crystal structure. The final refinement scheme for the S analogue was the same as that for the Se complex. The refinement converged at $R = 3.6$ and $R_w = 4.3$.

Results and Discussion

$Si(SC_6H_5)_4$ and $Si(SeC_6H_5)_4$ are isomorphous. Cell constants and other crystallographic data are presented in Table I. Figure 1 shows the molecular structure of $Si(SC_6H_5)_4$, an identical labeling scheme was used for the Se analogue. The atomic positions are summarized in Table II. Table III compiles the ^{29}Si NMR chemical shifts and relates this information to liquid and solid-state NMR data available in the literature on other compounds bearing $SiS_{4/2}$ and $SiSe_{4/2}$ structural environments.[9]

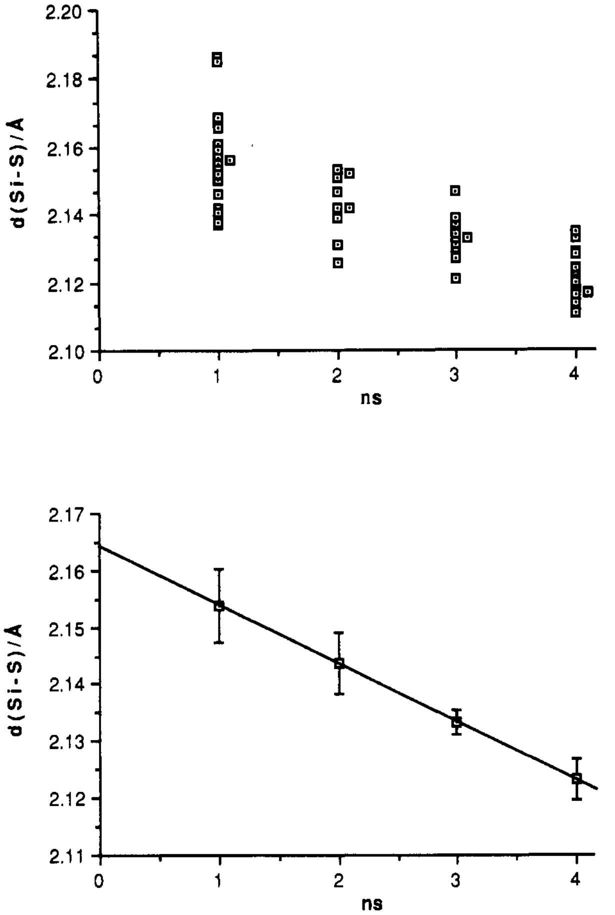

Figure 2. Top: Dependence of the Si–S distance on the number of sulfur ligands bonded to silicon, n_s. This compilation includes all data published in the literature excluding the polysilanes of ref 30, which show large variations in Si–S bond lengths due to internal mobility, and Si–S bonds involving Si atoms bonded to negatively charged S^- substituents. Some data points have been displaced sideways for clarity. Bottom: Correlation of the average Si–S bond lengths obtained from the data in Table III (weighted by their occurrences in the corresponding crystal structures) with n_s. Error bars indicate the 95% confidence intervals defined by the scatter among the reported values.

Table IV compares the Si–Ch bond lengths and the Si–Ch–C bond angles (Ch = S, Se) to the data previously reported in the literature on other silicon–chalcogen compounds.[10-28] The majority of Si–S bonds are substantially shorter than the sum of the covalent radii (2.19 Å), which is generally ascribed to a pπ–dπ back-bonding interaction. The Si–S bond lengths in $Si(SC_6H_5)_4$

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are comparable to those in SiS_2 and $Si(S_2C_2H_4)_2$, to our knowledge the only crystal structures of uncharged complexes previously reported, in which silicon is bonded to four sulfur ligands.[11] In addition to these uncharged compounds, structural data can be found in the literature on the $(C_6H_5S)_3SiS^-$ monoanion,[26] the dianion $Si_4S_6(SC_6H_5)_2(S^-)_2$,[26] and a variety of inorganic polyanions ($Si_4S_{10}^{4-}$,[31] $Si_2S_7^{6-}$,[32] and SiS_4^{4-} [33–41]). These data generally show a further shortening of the Si–S bond length to the sulfur atom bearing the negative charge and a concomitant lengthening of the other Si–S bonds. This induced asymmetry in the π-electron distribution is especially evident when we are comparing our data on $Si(SC_6H_5)_4$ with those published for the $Si(SC_6H_5)_3S^-$ monoanion.[26] A more detailed inspection of all the Si–S bond length data involving Si atoms bonded to only uncharged sulfur atoms reveals that there is a systematic trend towards increased Si–S bond lengths as n_s, the number of sulfur ligands at the silicon site, decreases from 4 to 1. Figure 2 shows the total number of data published in the literature as well as the averaged values of *d*(Si–S) weighted by their occurrence in the respective crystal structures. To check whether the trend is statistically significant, for each group of compounds representing a certain n_s value, standard deviations and 95% confidence intervals were calculated on the basis of the scatter in their occurrences. These 95% confidence intervals are included as error bars in Figure 2, which shows that with the exception of $n_s = 1/n_s = 2$ the confidence intervals do not overlap. The trend observed here closely parallels the effect previously discerned for Si–F bond lengths in the series $(CH_3)_nSiF_{4-n}$ $(0 \leq n \leq 3)$.[42] While the authors of that study hold polar contributions responsible for the effect on the Si–F bond, bond length shortening for Si–S bonds is usually discussed in terms of increased bond order due to pπ–dπ back-bonding.[26] Following this argument, we conclude that this contribution to the Si–S bond increases with n_s.

The Si–S–C bond angle in $Si(SC_6H_5)_4$ falls into the usual range near 100° previously known from similar structures, but is decidedly different from the larger values known to occur in a number of (((trimethylsilyl)sulfanyl)alkylidene)phosphane derivatives.[23–25]

Crystallographic reference data for our studies of $Si(SeC_6H_5)_4$ are virtually nonexistent. To the best of our knowledge, the Si–Se–C bond angle is the first such angle reported in the literature. The Si–Se bond length is close to the value of 2.275 Å in crystalline $SiSe_2$ and close to the sum of the covalent radii, indicating that π-bonding contributions to the Si–Se bonds can be considered negligible.

The ^{29}Si MAS-NMR spectra reveal huge chemical shift differences between $Si(SC_6H_5)_4$ and SiS_2 and between $Si(SeC_6H_5)_4$ and $SiSe_2$, respectively. As previously discussed,[43] ^{29}Si chemical shifts in silicates and zeolites are sensitively dependent on the s character of the neighboring oxygen atoms, which is reflected in the Si–O–X bond angle (X = Si, Al). Although the detailed nature of the relationship may be a different one in silicon–sulfur and –selenium compounds, the ^{29}Si chemical shifts are presumably also dependent on the hybridization state of the chalcogen atom. The structures of crystalline SiS_2 and $SiSe_2$ consist of four-membered Si–Ch–Si–Ch (Ch = S, Se) rings,[10] which are interconnected to form one-dimensional chains of edge-sharing $SiCh_{4/2}$ tetrahedra. The Si–Ch–Si angles are extremely small in these structures (around 90°), providing a rationalization for the unusual chemical shifts encountered in these compounds. Similar upfield shifts due to the presence of four-membered Si–S–Si–S rings have been observed in related systems.[44]

Inspection of Table III reveals further that the ^{29}Si resonance of $Si(SC_6H_5)_4$ is significantly downfield from that of other $SiS_{4/2}$ species that do not engage in four-membered rings. We attribute this effect to the influence of the second nearest-neighbor atoms (carbon for our compound, vs metal cations for the reference compounds). Chemical shift differences of similar direction and magnitudes are encountered when comparing the ^{29}Si NMR shifts of various $Si(OR)_4$ compounds with SiO_2.[45]

Further preparative, crystallographic, and solid-state NMR studies of silicon tetrathiolates and tetraselenolates that might function as connectivity models in silicon chalcogenide glasses are currently in progress.

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Supplementary Material Available: For $Si(SeC_6H_5)_4$ and $Si(SC_6H_5)_4$, tables of complete crystallographic data, calculated atomic positions for hydrogen atoms, isotropic and anisotropic temperature factors, and complete bond distances and angles, a crystal packing diagram for $Si(SPh)_4$, and a table of mass spectroscopic data (12 pages); tables of observed and calculated structure factors for $Si(SeC_6H_5)_4$ and $Si(SC_6H_5)_4$ (12 pages). Ordering information is given on any current masthead page.

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