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Preparation and Structural Characterization of $(Me_3SiNSN)_2Se$, a New Synthon for Sulfur–Selenium Nitrides

Jari Konu,[†] Arto Maaninen,[†] Katja Paananen,[†] Petri Ingman,[†] Risto S. Laitinen,*,[†] Tristram Chivers,[‡] and Jussi Valkonen[§]

*Departments of Chemistry, University of Oulu, P.O. Box 3000, 90014 University of Oulu, Finland,
University of Calgary, 2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4, and
University of Jyväskylä, P.O. Box 35, 40351 Jyväskylä, Finland*

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The reaction of $(Me_3SiN)_2S$ with $SeCl_2$ (2:1 ratio) in CH_2Cl_2 at –70 °C provides a route to the novel mixed selenium–sulfur–nitrogen compound $(Me_3SiNSN)_2Se$ (**1**). Crystals of **1** are monoclinic and belong the space group $P2_1/c$, with $a = 7.236(1)$ Å, $b = 19.260(4)$ Å, $c = 11.436(2)$ Å, $\beta = 92.05(3)°$, $V = 1592.7(5)$ Å^3, $Z = 4$, and $T = –155(2)$ °C. The NSNSeNSN chain in **1** consists of Se–N single bonds (1.844(3) Å) and S═N double bonds (1.521(3)–1.548(3) Å) with syn and anti geometry at the N═S═N units. The N–Se–N bond angle is 91.8(1)°. The EI mass spectrum shows a molecular ion with good agreement between the observed and calculated isotopic distributions. The ^{14}N NMR spectrum exhibits two resonances at –65 and –77 ppm. Both ^{13}C and ^{77}Se NMR spectra show single resonances at 0.83 and 1433 ppm, respectively. The reaction of **1** with an equimolar amount of $SeCl_2$ produces 1,5-$Se_2S_2N_4$ (**2**) in a good yield, and that of $(Me_3SiNSN)_2S$ with SCl_2 affords S_4N_4 (**3**), but the reactions of $(Me_3SiNSN)_2Se$ with SCl_2 and $(Me_3SiNSN)_2S$ with $SeCl_2$ result in the formation of a mixture of **2** and **3**. A likely reaction pathway involves the intermediate formation of E_2N_2 fragments (E = S, Se).

Introduction

Bis(trimethylsilylimino)sulfane $(Me_3SiN)_2S$[1] has played an important role in the development of chalcogen−nitrogen chemistry by providing NSN fragments to a variety of cyclic and acyclic main-group compounds and transition-metal complexes.[2] For example, $(Me_3SiN)_2S$ has been used to prepare thiazyl compounds of different chain lengths. These compounds mimic the structure of the $(SN)_x$ polymer.[15]

Treating $(Me_3SiN)_2S$ with SCl_2 affords $(Me_3SiNSN)_2S$, the synthetic utility of which can be exemplified by a convenient preparation of S_4N_4[1] or by the production of palladium complexes containing S−N chelating ligands.[16] $(Me_3SiNSN)_2S$ and its derivatives have also served as models in the MO study of the electronic structure of the polymeric $(SN)_x$ chain.[17]

Selenium−nitrogen chemistry has seen much slower development than has sulfur−nitrogen chemistry because of the lack of suitable reagents. The selenium analogue of $(Me_3SiN)_2S$ is unstable[18] and, therefore, of limited utility.[19]

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* Corresponding author. E-mail: risto.laitinen@oulu.fi.

[†] University of Oulu.

[‡] University of Calgary.

[§] University of Jyväskylä.

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Progress in selenium−nitrogen chemistry is largely due to reagents such as $[(Me_3Si)_2N]_2E$ (E = S, Se).[20−23]

In this contribution, we describe in detail the preparation of $(Me_3SiNSN)_2Se$ as a part of the systematic investigation of new selenium−nitrogen compounds that may be useful in synthetic applications. The product was characterized by X-ray crystallography, ^{77}Se, ^{14}N, and ^{13}C NMR spectroscopy, and mass spectrometry. The reactions of $(Me_3SiNSN)_2Se$ with ECl_2 (E = S,Se) have also been investigated.

Experimental Section

General Procedures. All reactions and manipulations of air- and moisture-sensitive reagents were carried out under an argon atmosphere that was passed through P_4O_{10}. SO_2Cl_2 and SCl_2 (Aldrich) were used without further purification. Bis(trimethylsilylimino)sulfane, $(Me_3SiN)_2S$, was prepared from $[(Me_3Si)_2N]_2S$ with an equimolar amount of SO_2Cl_2.[24] $[(Me_3Si)_2N]_2S$ was prepared from $(Me_3Si)_2NH$ using the method of Wolmershäuser et al.[25] and purified by distillation. $(Me_3SiNSN)_2S$ was prepared in hexane by the procedure described by Kelly et al.[16] Selenium dichloride, $SeCl_2$, was prepared from elemental selenium and SO_2Cl_2.[26] The solvents were dried by distillation under a nitrogen atmosphere prior to use. Dichloromethane was dried over P_4O_{10}, and THF was dried over Na/benzophenone.

Spectroscopic Methods. The ^{13}C, ^{14}N, and ^{77}Se NMR spectra were recorded in CH_2Cl_2 on a Bruker DPX 400 spectrometer operating at 100.623, 28.909, and 76.406 MHz, respectively. The spectral widths were 30.30, 14.49, and 99.01 kHz, yielding the respective resolutions of 0.92, 7.08, and 1.51 Hz/data point. The pulse widths were 4.00 μs for ^{13}C, 12.0 μs for ^{14}N, and 6.70 μs for ^{77}Se, corresponding to nuclear tip angles of 36, 44, and 46°, respectively. The ^{13}C accumulations contained 50−1000 transients, those for ^{14}N, 9000−30 000, and those for ^{77}Se 200−18 000 transients. All spectra were recorded unlocked. The ^{14}N NMR chemical shifts are reported relative to CH_3NO_2. All ^{77}Se NMR spectra are referenced externally to a saturated solution of SeO_2. The chemical shifts are reported relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$].

^{77}Se MAS-NMR spectra of solid 1,5-$Se_2S_2N_4$ (**2**) were recorded at 57.328 MHz on a Bruker DSX300 spectrometer. A 7 mm zirconia rotor with a Kel-F cap was used with spin rates of 3.5−4.5 kHz. The spectral width was 80 kHz, and the pulse width was 1.67 μs, corresponding to the nuclear tip angle of 30°. The tip angle and relaxation delay (ca. 1 s) were optimized to reach the best signal-to-noise ratio during the accumulation. Typically, 32 000 transients were required to obtain acceptable spectra. All measurements were made at room temperature. The spectra were referenced to diphenyl diselenide that gives two series of signals with isotropic shifts of 425 and 350 ppm.[27] The spectral simulation was carried out using the program *WIN-MAS* supplied by Bruker.

EIMS was recorded by using a Kratos MS 80 spectrometer at 12 eV of electron energy.

Preparation of $(Me_3SiNSN)_2Se$ (1). A solution of $SeCl_2$ in THF (3 mL) was prepared from elemental selenium (0.079 g, 1.00 mmol) and SO_2Cl_2 (0.135 g, 1.00 mmol) and was added immediately into 20 mL of a dichloromethane solution of $(Me_3SiN)_2S$ (0.413 g, 2.00 mmol) at −70 °C under an argon atmosphere. Stirring was continued overnight, during which time the reaction mixture was allowed to warm slowly to room temperature. The resulting mixture was filtered, and the orange solution was evaporated to dryness under vacuum. The reddish-yellow solid was dissolved in hexane and filtered to remove traces of $Se_2S_2N_4$ that are produced as a byproduct. The orange solution was evaporated under vacuum to 20% of its original volume. Needle-shaped yellow crystals of $(Me_3SiNSN)_2Se$ (**1**) were obtained by slow evaporation of the solvent in an argon atmosphere. The yield was 0.225 g (65%). Crystals of **1** were used for the mass spectrometric, ^{13}C, ^{14}N, and ^{77}Se NMR spectroscopic, and crystallographic characterization of the product.

Reaction of $(Me_3SiNSN)_2Se$ with $SeCl_2$. *Caution! Dry $Se_2S_2N_4$ is explosive under the influence of heat or mechanical stress. The product should be stored and handled under hydrocarbon solvents and its preparation limited to amounts of <1.0 g. A polycarbonate blast shield should be employed, and the experimenter should wear heavy-duty gloves and ear protection.*

$(Me_3SiNSN)_2Se$ (0.346 g, 1.00 mmol) was dissolved in dichloromethane (20 mL), and $SeCl_2$ (0.150 g, 1.00 mmol) in THF (3 mL) was added dropwise at −70 °C. The reaction mixture was stirred overnight and allowed to warm slowly to room temperature to give a dark red, slightly soluble precipitate. The yield of 1,5-$Se_2S_2N_4$ (**2**) was 0.203 g (73%). NMR: ^{14}N (CH_2Cl_2, 25°, δ) −238; ^{77}Se (CH_2Cl_2, 25 °C, δ) 1417.[28] The crystalline solid was used in the ^{77}Se MAS-NMR study.

Reaction of $(Me_3SiNSN)_2Se$ with SCl_2. $(Me_3SiNSN)_2Se$ (0.346 g, 1.00 mmol) was dissolved in dichloromethane (20 mL), and SCl_2 (0.103 g, 1.00 mmol) in THF (3 mL) was added dropwise at −70 °C under an argon atmosphere. The reaction mixture was stirred overnight and allowed to warm slowly to room temperature to give a dark red precipitate (0.096 g) and a slightly reddish solution. NMR: ^{14}N (CH_2Cl_2, 25 °C, δ) −238 and −256 ; ^{77}Se (CH_2Cl_2, 25 °C, δ) 1417.

Reaction of $(Me_3SiNSN)_2S$ with $SeCl_2$. $(Me_3SiNSN)_2S$ (0.298 g, 1.00 mmol) was dissolved in dichloromethane (20 mL), and $SeCl_2$ (0.150 g, 1.00 mmol) in THF (3 mL) was added dropwise at −70 °C under an argon atmosphere. The reaction mixture was stirred overnight and allowed to warm slowly to room temperature to give a dark red precipitate (0.112 g) and a slightly reddish solution. NMR: ^{14}N (CH_2Cl_2, 25 °C, δ) −238 and −256; ^{77}Se (CH_2Cl_2, 25 °C, δ) 1417.

X-ray Crystallography. Crystal data for $(Me_3SiNSN)_2Se$ (**1**) are given in Table 1. Diffraction data were collected on a Nonius Kappa CCD diffractometer at −155 °C using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by recording 360 frames via φ-rotation ($\Delta\varphi = 1°$; two times at 40 s per frame). There were 3013 unique reflections ($2.07 < \theta < 25.68°$), of which 2534 had $I > 2.00\sigma(I)$. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied to the net intensities. The structure was solved by direct methods using

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Table 1. Crystal Data and Structure Refinement for $(Me_3SiNSN)_2Se$

empirical formula	$C_6H_{18}N_4S_2SeSi_2$
fw, g/mol	345.50
cryst syst	monoclinic
a (Å)	7.236(1)
b (Å)	19.260(4)
c (Å)	11.436(2)
β (deg)	92.05(3)
V (Å^3)	1592.7(5)
Z	4
space group	$P2_1/c$
T (°C)	−155(2)
λ (Mo Kα) (Å)	0.71073
ρ_{calc} (g/cm^3)	1.441
μ (mm^{-1})	2.751
F(000)	704
cryst size (mm^3)	0.40 × 0.20 × 0.20
R indices [$I > 2\sigma(I)$][a]	0.0354
wR2 (all data)[b]	0.0799

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$, [b] $w = [\sigma^2(F_o^2) + (0.0318P)^2 + 1.75P]^{-1}$ where $P = \{\max(F_o^2, 0) + 2F_c^2\}/3$

SHELXS-97[30] and refined using *SHELXL-97*.[31] The scattering factors for the neutral atoms were those incorporated in the programs.

Results and Discussion

Preparation, Spectroscopic Characterization, and X-ray Structure of $(Me_3SiNSN)_2Se$ (1). The reaction of $(Me_3SiN)_2S$ with $SeCl_2$ in CH_2Cl_2 is a convenient route for the synthesis of $(Me_3SiNSN)_2Se$ (**1**). The product was obtained as yellow needle-shaped crystals in ca. 65% yield.

$$2(Me_3SiN)_2S + SeCl_2 \rightarrow \underset{\mathbf{1}}{Me_3SiNSNSeNSNSiMe_3} + 2Me_3SiCl \quad (1)$$

The mass spectrum of **1** is consistent with the molecular formula of $(Me_3SiNSN)_2Se$. The ion of highest mass (the highest relative intensity of the isotopic distribution pattern was observed at m/z 346) was assigned to the molecular ion on the basis of the comparison between the calculated and observed isotopic distributions, which are in excellent agreement with each other. The fragmentation pattern is also consistent with the molecular formula of **1**.

The ^{13}C, ^{14}N, and ^{77}Se NMR spectra of **1** were recorded in CH_2Cl_2. The ^{14}N NMR spectrum shows two resonances at −65 and −77 ppm that lie in the same region as does the ^{14}N chemical shift of −54.2 ppm reported for $(Me_3SiN)_2S$ that also contains a N=S=N fragment.[32] Only one resonance was observed in both ^{13}C and ^{77}Se NMR spectra. The ^{13}C chemical shift of **1** is 0.83 ppm, and the ^{77}Se chemical shift was observed at 1433 ppm. The former resonance is typical for the Me_3Si- group, and the latter lies in the region expected for a selenium(II) atom bound to two nitrogen atoms.[33]

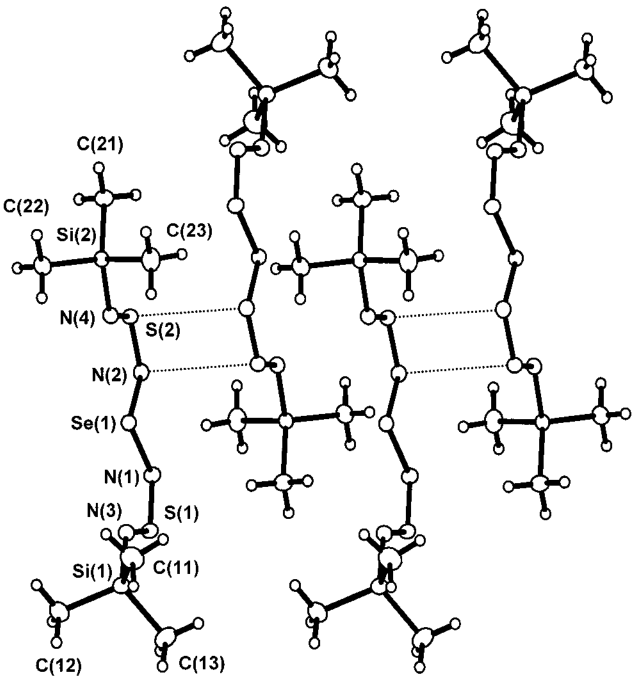

Figure 1. Molecular structure of $(Me_3SiNSN)_2Se$. Thermal ellipsoids are drawn at 50% probability level.

Table 2. Selected Bond Lengths and Bond Angles for $(Me_3SiNSN)_2Se$.

	Bond Lengths (Å)		
Se(1) − N(1)	1.844(3)	S(2) − N(2)	1.548(3)
Se(1) − N(2)	1.844(3)	S(2) − N(4)	1.523(3)
S(1) − N(1)	1.541(2)	Si(1) − N(3)	1.755(3)
S(1) − N(3)	1.521(3)	Si(2) − N(4)	1.757(3)
	Bond Angles (deg)		
N(1) − Se(1) − N(2)	91.8(1)	N(2) − S(2) − N(4)	113.4(1)
Se(1) − N(1) − S(1)	114.3(2)	S(1) − N(3) − Si(1)	128.8(2)
Se(1) − N(2) − S(2)	112.9(2)	S(2) − N(4) − Si(2)	126.4(2)
N(1) − S(1) − N(3)	113.9(2)		

The molecular structure of **1** with the atomic numbering scheme is shown in Figure 1. Bond lengths and bond angles are summarized in Table 2. The Se−N distance of 1.844(3) Å is consistent with the single-bond lengths of 1.827(5) and 1.869(2) Å observed for OSN−Se−NSO[22] and $(Me_3Si)_2N-Se-N(SiMe_3)_2$,[23] respectively. The N−Se−N bond angle of 91.8(1)°, however, is significantly smaller than the angle of 108.0(1)° in $(Me_3Si)_2N-Se-N(SiMe_3)_2$,[23] but it is similar to that of 92.0(2)° in OSN−Se−NSO.[22] The steric crowding of the trimethylsilyl groups probably opens the bond angle in $(Me_3Si)_2N-Se-N(SiMe_3)_2$. The four sulfur−nitrogen bond lengths (1.521(3)−1.548(3) Å) in **1** imply the presence of double bonds[34] and are comparable to those observed in $(^tBuNSN)_2S$, (1.50(4)−1.56(2) Å).[36] The two N=S=N bond

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(33) The ^{77}Se chemical shifts of 1,5-$Se_2S_2N_4$ in CS_2 at 1418 ppm[29] and $[(Me_3Si)_2N]_2Se$ in CH_2Cl_2 at 1130 ppm[23] have been reported. The four large Me_3Si groups in $[(Me_3Si)_2N]_2Se$ fold around selenium and probably shield the nucleus, explaining why the ^{77}Se chemical shift lies at an abnormally high field.

(34) The S=N double-bond length of 1.516(6) Å is observed in $(ONS)_2Se$ by X-ray crystallography,[22] and that of 1.536(3) Å is observed in $(Me_3SiN)_2S$ by electron diffraction.[35]

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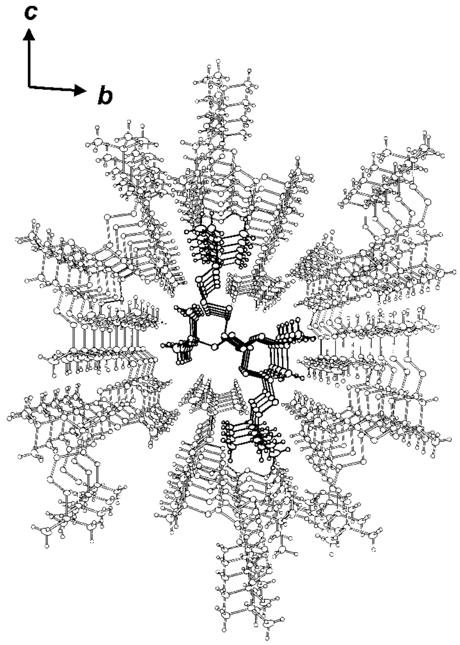

Figure 2. Stacking of interlocking $(Me_3SiNSN)_2Se$ molecules in the lattice.

angles of 113.4(1) and 113.9(2)° in **1** are also in agreement with those observed in $(^tBuNSN)_2S$, (110.(1) and 114(1)°).[36]

The SiNSNSeNSNSi chain in **1** is approximately planar and shows syn,anti geometry at the N=S=N units. The molecular structure of $(Me_3SiNSN)_2S$, the sulfur analogue of **1**, is unknown; however, the related chain $(^tBuNSN)_2S$ exhibits the same conformational features as does **1**.[36] Recent DFT calculations on R−N=S=N−R[37] have shown that the syn,anti isomer is indeed the most stable of the three possible isomers, and this conformation is also found for $(Me_3SiN)_2S$ by electron diffraction.[35] It is worth noting that the OSNSeNSO chain is also planar[22] and exhibits a conformation similar to that of the NSNSeNSN chain in **1**.

As seen in Figure 2, the packing of the lattice consists of stacks of interlocking molecules with only van der Waals interactions between the stacks. Within the stacks, the closest contacts are found between S(2) and N(2) that link adjacent molecules into pairs (see Figure 1). This interaction, however, is also very weak because the S···N distance of 3.342(3) Å is close to the sum of van der Waals radii of 3.39 Å for sulfur and nitrogen.[38]

Synthesis and Solid-State ^{77}Se NMR Spectrum of 1,5-$Se_2S_2N_4$. We have previously reported that 1,5-$Se_2S_2N_4$ (**2**) can be prepared in high yield by two different routes: (a) from $[(Me_3Si)_2N]_2S$ and $SeCl_4$ and (b) from $[(Me_3Si)_2N]_2Se$ with equimolar amounts of SCl_2 and SO_2Cl_2.[29] We have now observed that **2** can also conveniently be prepared by the treatment of $(Me_3SiNSN)_2Se$ (**1**) with $SeCl_2$ in CH_2Cl_2. The product was identified as 1,5-$Se_2S_2N_4$ by ^{14}N and ^{77}Se NMR spectroscopy.[29]

$$(Me_3SiNSN)_2Se + SeCl_2 \rightarrow \underset{\mathbf{2}}{1,5\text{-}Se_2S_2N_4} + 2Me_3SiCl \quad (2)$$

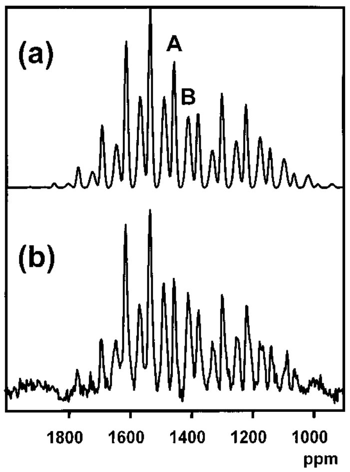

Figure 3. ^{77}Se MAS spectrum of $Se_2S_2N_4$ at a spinning rate of 4.5 kHz. (a) simulated spectrum and (b) experimental spectrum. Isotropic lines are indicated by A and B.

The base-corrected ^{77}Se MAS-NMR spectrum of 1,5-$Se_2S_2N_4$ at a spinning rate of 4.5 kHz is shown in Figure 3, together with the simulated spectrum. It could be inferred from the simulated spectrum that there are two series of spinning sideband patterns A and B, with the respective isotropic chemical shifts lying at 1455 and 1409 ppm, respectively.[39] The line widths of peaks in series A and B are 730 and 1060 Hz, respectively. The isotropic values were confirmed by recording the spectrum at different spinning rates. These solid-state isotropic ^{77}Se chemical shifts are consistent with the chemical shift of 1418 ppm recorded for **2** in CS_2 solution.[29]

The two resonances in the ^{77}Se MAS-NMR spectrum can be assigned as follows. 1,5-$Se_2S_2N_4$ shows a cage structure[29] similar to those of S_4N_4[40−42] and Se_4N_4.[43,44] The 1,5-$Se_2S_2N_4$ molecule, however, can assume two different orientations in the lattice, and the crystal structure of **2** is therefore disordered, with sulfur and selenium statistically distributed over the chalcogen atom sites, resulting in four crystallographically different selenium atom sites.[45] The selenium atoms in these four chalcogen atom positions can be divided into two groups. The selenium atoms in positions E(1) and E(4) show two independent intermolecular close-contacts to nitrogen atoms, while those in E(2) and E(3) both exhibit only one selenium−nitrogen close-contact (see Figure 4).

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[45] It should be noted that β-Se_4N_4 is isomorphic with **2** and also has four crystallographically different selenium atoms.[44] It is possible that the disorder observed in the crystal structure of **2**[29] is not caused by the two different orientations of the 1,5-$Se_2S_2N_4$ molecule but is due to the existence of a solid solution between S_4N_4 and Se_4N_4. Crystallographic data alone cannot distinguish between these two alternatives. The mass spectrum as well as the Raman spectrum and normal coordinate analysis, however, have clearly demonstrated the formation of 1,5-$Se_2S_2N_4$.[29,46]

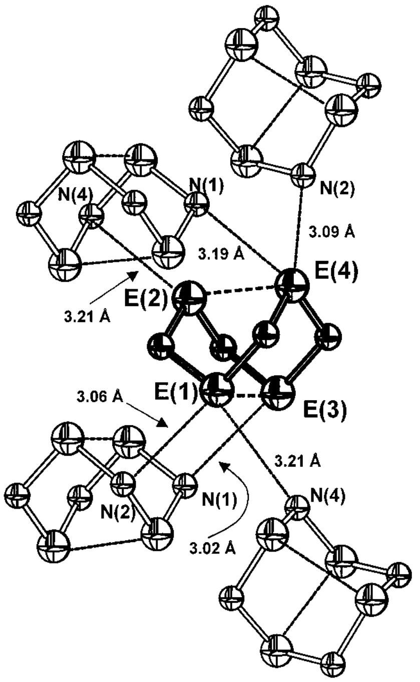


Figure 4. Intermolecular chalcogen···nitrogen interactions in 1,5-$Se_2S_2N_4$ based on the crystallographic data given in reference 29.

The broader B lines are attributed to the interaction of the selenium nucleus with two quadrupolar ^{14}N nuclei and are therefore assigned to the selenium atoms in positions E(1) and E(4). The narrower A lines are due to selenium atoms in positions E(2) and E(3), both with only one N···Se close contact. The differences in the environments of the selenium atoms within the two groups are very small and are therefore not expected to be resolved in the ^{77}Se MAS-NMR spectrum.

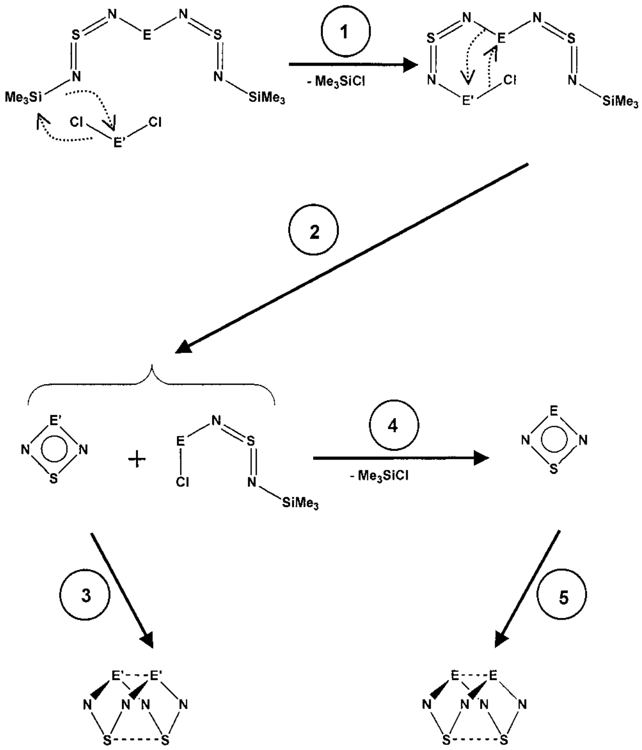
Reactions of $(Me_3SiNSN)_2E$ and $E'Cl_2$ (E, E′ = S or Se). The reaction between $(Me_3SiNSN)_2S$ and SCl_2 has been reported to produce S_4N_4[1] in a fashion similar to the synthesis of 1,5-$Se_2S_2N_4$ discussed above.

$$(Me_3SiNSN)_2S + SCl_2 \rightarrow S_4N_4 + 2Me_3SiCl \qquad (3)$$

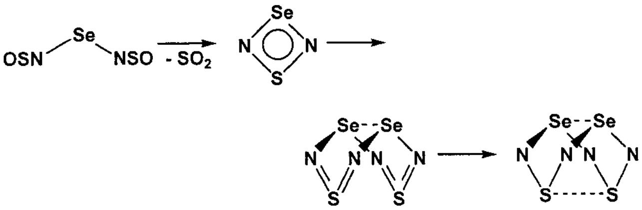
The reactions of $(Me_3SiNSN)_2Se$ with SCl_2 and $(Me_3SiNSN)_2S$ with $SeCl_2$ were therefore expected to produce the unknown eight-membered selenium−sulfur nitride, SeS_3N_4. However, both reactions afforded an equimolar mixture of 1,5-$Se_2S_2N_4$ and S_4N_4. Two resonances at −238 and −256 ppm were observed in the ^{14}N NMR spectra of both reaction solutions and can be assigned to 1,5-$Se_2S_2N_4$[29] and S_4N_4,[47] respectively. The single resonance observed at 1417 ppm in the ^{77}Se NMR spectra of both reaction solutions provides further verification of this assignment.

$$(Me_3SiNSN)_2E + E'Cl_2 \rightarrow$$
$$\tfrac{1}{2}1,5\text{-}Se_2S_2N_4 + \tfrac{1}{2}S_4N_4 + 2Me_3SiCl \qquad (4)$$
$$(E = S, E' = Se \text{ or } E = Se, E' = S)$$

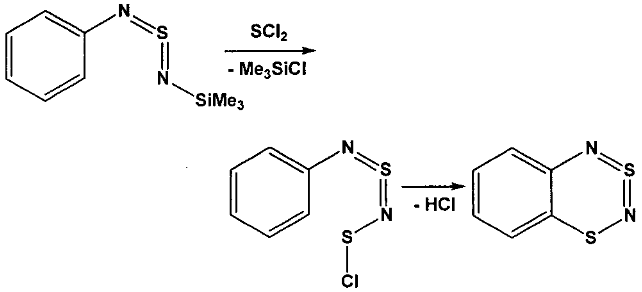
Scheme 1



Reaction Pathway. Haas et al.[22,48] have suggested that the decomposition of $Se(NSO)_2$ produces 1,5-$Se_2S_2N_4$ via a cyclic, four-membered intermediate:



The product distributions observed in the reactions of $(Me_3SiNSN)_2E$ and $E'Cl_2$ (E, E′ = S, Se) (see eqs 2−4) can be explained by a related pathway, as shown in Scheme 1. The reaction seems to be initiated by the cleavage of one Si−N bond in $(Me_3SiNSN)_2E$ by $E'Cl_2$, with elimination of Me_3SiCl and formation of $ClE'NSNENSNSiMe_3$. A similar type of intermediate formation has also been suggested for cyclocondensation of $PhNSNSiMe_3$:[49]



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(46) Maaninen, A.; Konu, J.; Laitinen, R. S.; Chivers, T.; Schatte, G.; Pietikäinen, J.; Ahlgrén, M. *Inorg. Chem.* **2001**, *40*, 3539.

(47) Chivers, T.; Oakley, R. T.; Scherer, O. J.; Wolmershäuser, G. *Inorg. Chem.* **1981**, *20*, 914.

Step 2 in Scheme 1 involves an intramolecular rearrangement, resulting in the formation of cyclic $E'SN_2$ and $ClENSNSiMe_3$. The dimerization of $E'SN_2$ (step 3) yields $E'_2S_2N_4$. Elimination of Me_3SiCl from $ClENSNSiMe_3$ (step 4) creates ESN_2, the dimerization of which yields $E_2S_2N_4$ (step 5). Thus, the reaction of $(Me_3SiNSN)_2Se$ and $SeCl_2$ affords only 1,5-$Se_2S_2N_4$, and that of $(Me_3SiNSN)_2S$ and SCl_2 produces only S_4N_4.[1,50] The dimerization of S_2N_2 to S_4N_4 is known to be catalyzed by nucleophiles.[5,51]

According to Scheme 1, the reaction of $(Me_3SiNSN)_2Se$ and $SeCl_2$ could also produce 1,3-$Se_2S_2N_4$, depending on the way the four-atomic intermediate $SeSN_2$ dimerizes. The ^{14}N and ^{77}Se NMR spectra, however, show no evidence of the presence of this isomer. The formation of the 1,3-isomer via steps 3 or 5 would require an eight-membered intermediate that contains an unstable $N{=}Se{=}N$ fragment,[18,52] rendering the formation of 1,3-$Se_2S_2N_4$ unlikely.

While the mutual dimerization of ESN_2 and $E'SN_2$ leads to the 1,5-isomers of $E_2S_2N_4$ and $E'_2S_2N_4$, respectively, the combination of ESN_2 with $E'SN_2$ should also be possible, affording a hybrid $EE'S_2N_4$. Therefore, the treatment of $(Me_3SiNSN)_2Se$ with SCl_2 or that of $(Me_3SiNSN)_2S$ with $SeCl_2$ could also yield SeS_3N_4 in addition to S_4N_4 and 1,5-$Se_2S_2N_4$. However, only an equimolar mixture of S_4N_4 and 1,5-$Se_2S_2N_4$ is observed. This result can be explained by assuming that step 4 in Scheme 1 is much slower than the dimerization (step 3). In that case, most of $E'SN_2$ will have dimerized to 1,5-$E'_2S_2N_4$ before significant amounts of ESN_2 are formed. The latter intermediate is then left to produce 1,5-$E_2S_2N_4$.

Conclusions

The novel $(Me_3SiNSN)_2Se$ chain compound has been prepared in good yield by the reaction of $(Me_3SiN)_2S$ with $SeCl_2$. The identification and characterization of this species have been carried out by X-ray crystallography, NMR spectroscopy, and mass spectrometry. While the reactions of $(Me_3SiNSN)_2S$ and SCl_2 or $(Me_3SiNSN)_2Se$ and $SeCl_2$ provide convenient routes to S_4N_4 and 1,5-$Se_2S_2N_4$, respectively, those of $(Me_3SiNSN)_2Se$ and SCl_2 or $(Me_3SiNSN)_2S$ and $SeCl_2$ result in the formation of equimolar mixtures of S_4N_4 and 1,5-$Se_2S_2N_4$. Neither SeS_3N_4 nor 1,3-$Se_2S_2N_4$ is observed as a product of these reactions.

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Supporting Information Available: X-ray crystallographic CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(48) Haas, A.; Pryka, M. *Chem. Ber.* **1995**, *128*, 11.

(49) Cordes, A. W.; Hojo, M.; Koenig, H.; Noble, M. C.; Oakley, R. T.; Pennington, W. T. *Inorg. Chem.* **1986**, *25*, 1137.

(50) In reaction 2, both ESN_2 and $E'SN_2$ have the composition $SeSN_2$, and in reaction 3, both ESN_2 and $E'SN_2$ have the composition S_2N_2. In reaction 2, both dimerization steps (steps 3 and 5 in Scheme 1) will lead to a final product with the composition $Se_2S_2N_4$. In reaction 3, both dimerization steps will lead to a final product with the composition S_4N_4.

(51) Goehring, M.; Voigt, D. *Z. Anorg. Allg. Chem.* **1956**, *285*, 181.

(52) The ab initio calculations performed on the six-atom ring molecules $Se_xS_{4-x}N_2$ ($x = 0-4$)[24] have shown that, for a given composition, isomers with a $N{=}Se{=}N$ fragment lie at higher energy than do those containing a $N{=}S{=}N$ fragment.