2170 *Inorg. Chem.* **1997,** *36,* 2170−2177

Theoretical and Experimental Studies of Six-Membered Selenium−Sulfur Nitrides $Se_xS_{4-x}N_2$ ($x = 0-4$). Preparation of S_4N_2 and SeS_3N_2 by the Reaction of Bis[bis(trimethylsilyl)amino]sulfane with Chalcogen Chlorides

Arto Maaninen,[1a] Jari Siivari,[1a] Reijo J. Suontamo,[1b] Jari Konu,[1a] Risto S. Laitinen,*,[1a] and Tristram Chivers*,[1c]

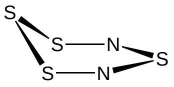
Departments of Chemistry, University of Oulu, Linnanmaa, 90570 Oulu, Finland,
University of Jyväskylä, P.O. Box 35, 40351 Jyväskylä, Finland, and The University of Calgary,
2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4

Received November 8, 1996⊗

The reaction of $[(Me_3Si)_2N]_2S$ with equimolar amounts of SCl_2 and S_2Cl_2 produces S_4N_2 in a good yield. The reaction of $[(Me_3Si)_2N]_2S$ with a 3:1:1 mixture of S_2Cl_2, Se_2Cl_2, and $SeCl_4$ yields a dark brown-red insoluble material that was inferred to be mainly $\overline{\mathrm{SSeSNSN}}$ on the basis of the elemental analysis, mass spectroscopy, vibrational analysis, and NMR spectroscopy. Attempts to prepare selenium-rich species resulted in the formation of elemental selenium or $Se_3N_2Cl_2$. The experimental work was supported by *ab initio* MO calculations which establish the structural and stability relationships of the different members of the series 1,3-$Se_xS_{4-x}N_2$ ($x = 0-4$). Full geometry optimization was carried out for each molecular species using the polarized split-valence MIDI-4* basis sets. The effects of electron correlation were taken into account involving the second-order Møler−Plessett perturbation theory. Each molecule was found to lie in an approximate half-chair conformation that is well established for 1,3-S_4N_2 (i.e., interacting planar NEN and EEE fragments; E = S, Se). The bond parameters agree well with experimental information where available. Whereas the lengths of the bonds in the NEEEN fragment approach those of the single bonds, the bonds in the NEN fragment show marked double bond character. The stabilities of the molecules decrease expectedly with increasing selenium content as judged by the total binding energy at the MP2 level of theory. Within a given chemical composition, isomers containing a N=Se=N unit lie higher in energy than those containing a N=S=N unit. These results may explain why selenium-rich $Se_xS_{4-x}N_2$ molecules have not been isolated.

Introduction

Tetrasulfur dinitride has long been known as a source of the red color present in many reaction mixtures when sulfur-nitrogen compounds are prepared.[2] The elucidation of the molecular structure of S_4N_2 had long been problematic because of the instability and the low melting point of the species. Early spectroscopic studies established that the molecule is cyclic with two equivalent nitrogen atoms, but the conformation of the ring remained unclear.[2] CNDO/2 studies of Adkins and Turner[3] favored a planar molecule, whereas the *ab initio* calculations of Palmer *et al.*[4] indicated a half-chair conformation. It was only in the beginning of 1980s that the low-temperature crystal structure established unequivocally that S_4N_2 is cyclic and lies in a half-chair conformation:[5]



The existence of selenium-containing analogues of S_4N_2 has been under debate. Dehnicke *et al.*[6] reported the preparation of Se_4N_2 by the reaction of dichlorodiselane with trimethylsilyl azide in dichloromethane. Se_4N_2 was obtained as a black powder that was said to be stable up to 80 °C. The identification was based on the assignment of the IR spectrum by comparison with that of 1,3-S_4N_2, and with the frequencies calculated for Se_4N_2 at the Hartree−Fock (HF) level of theory utilizing the 3-21G*. The existence of Se_4N_2 was further rationalized by the formation of 2:1 and 1:1 adducts with $SnCl_4$ and $TiCl_4$, respectively.[7] The reported stability of Se_4N_2, however, was incompatible with the earlier observation that the reaction of dichlorodiselane with trimethylsilyl azide in dichloromethane produces an explosive blue-black Se−N compound.[8] Indeed, a reinvestigation of this reaction showed the product to be unstable $Se_3N_2Cl_2$.[9]

It has been established that the reactions of $[(Me_3Si)_2N]_2E$ (E = S, Se) with chalcogen chlorides produce a wide variety of chalcogen−nitrogen species. For instance, the reaction of $[(Me_3Si)_2N]_2Se$ and $SeCl_4$ results in the formation of Se_4N_4.[10] Our preliminary results have shown that the analogous reaction of $[(Me_3Si)_2N]_2S$ with SCl_2 and SO_2Cl_2 leads expectedly to the

---

⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1997.

(1) (a) University of Oulu. (b) University of Jyväskylä. (c) The University of Calgary.

(2) For reviews on S−N compounds, see: (a) Chivers, T. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press, Inc.: London, 1987; Vol. 2, pp 793−869. (b) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, *36*, 299.

(3) Adkins, R. R.; Turner, A. G. *J. Am. Chem. Soc.* **1978**, *100*, 1383.

(4) Palmer, M. H.; Wheeler, J. R.; Findlay, R. H.; Westwood, N. P. C.; Lau, W. M. *J. Mol. Struct.* **1981**, *86*, 193.

(5) (a) Chivers, T.; Codding, P. W.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1981**, 584. (b) Chivers, T.; Codding, P. W.; Laidlaw, W. G.; Liblong, S. W.; Oakley, R.T.; Trsic, M. *J. Am. Chem. Soc.* **1983**, *105*, 1186. (c) Small, R. W. H.; Banister, A. J.; Hauptman, Z. V. *J. Chem. Soc., Dalton Trans.* **1981**, 2188.

(6) Dehnicke, K.; Schmock, F.; Köhler, K. F.; Frenking, G. *Angew. Chem.* **1991**, *103*, 564; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 577.

(7) Vogler, S.; Schafer, M.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1991**, *606*, 73.

(8) Kennett, F. A.; MacLean, G. K.; Passmore, J.; Rao, M. N. S. *J. Chem. Soc., Dalton Trans.* **1982**, 851.

(9) (a) Siivari, J.; Chivers, T.; Laitinen, R. S. *Angew. Chem.* **1992**, *104*, 1539; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1518. (b) Siivari, J.; Chivers, T.; Laitinen, R. S. *Inorg. Chem.* **1993**, *32*, 4391.

(10) Siivari, J.; Chivers, T.; Laitinen, R. S. *Inorg. Chem.* **1993**, *32*, 1519.

S0020-1669(96)01357-2 CCC: $14.00

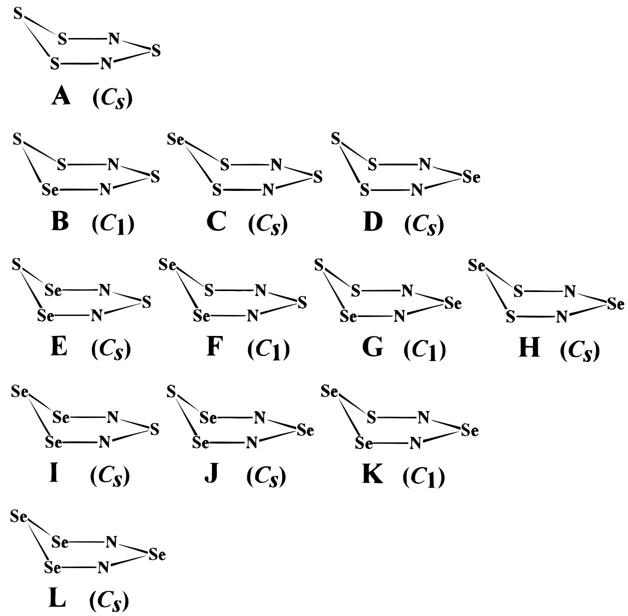


Figure 1. Heterocyclic $Se_xS_{4-x}N_2$ ($x = 0-4$) molecules, their molecular symmetries, and the abbreviated notation.

formation of S_4N_4.[11] Furthermore, the treatment of $[(Me_3Si)_2N]_2S$ with SCl_2 and S_2Cl_2 produces S_4N_2 in a good yield.[11] The reaction route is quite dependent on the molar ratio of the reactants. By suitable adjustment of the chalcogen to chlorine ratio, chlorine-containing species of the types $E_3N_2Cl_2$ and $(E_3N_2Cl)_2$ are formed.[9,11,12] Similar products can also be prepared by the direct reaction of $(Me_3Si)_2NLi$ with chalcogen chlorides.[10,11]

The present study is a part of our interest in the mixed six-membered chalcogen nitrides $Se_xS_{4-x}N_2$.[13] We report here a convenient synthesis of S_4N_2 from $[(Me_3Si)_2N]_2S$, SCl_2, and S_2Cl_2. The reaction of $[(Me_3Si)_2N]_2S$ with mixtures of sulfur and selenium chlorides is shown to provide a way to introduce selenium into the six-membered ring. The reaction products are identified by vibrational analysis, NMR, and mass spectroscopy. The synthetic work is supported by *ab initio* molecular orbital calculations on all members of the heterocyclic series $Se_xS_{4-x}N_2$ ($x = 0-4$; see Figure 1), which were carried out in order to establish the structural and stability relationships as a function of the selenium content in the molecule.[14]

Ab Initio Molecular Orbital Calculations

All MO calculations were carried out with Gaussian 92[16] involving MIDI-4* basis sets[17] augmented by *d*-polarization functions.[18] The gradient techniques were employed in the geometry optimization of all 12 possible isomers. A second-order Møller−Plesset correction for electron correlation[20] was performed using the optimized geometries. The fundamental vibrations were calculated for the optimized geometries at the HF level of theory. This serves to establish the nature of the stationary points and helps in the assignments of the observed IR and Raman spectra. The calculated wavenumbers have been scaled by 0.89 to eliminate the systematic errors.[21] The internal coordinates of the six-membered chalcogen−nitrogen rings are defined in Figure 2.

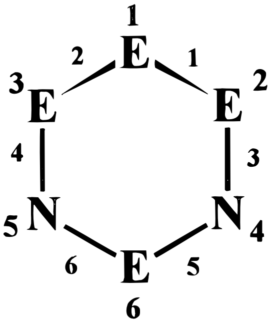


Figure 2. Numbering of bonds and atoms in $Se_xS_{4-x}N_2$.

Experimental Section

General Considerations. All reactions were carried out under a nitrogen atmosphere. $(Me_3Si)_2NH$ (Aldrich), *n*-butyllithium (1.6 M in hexanes, Aldrich), and elemental sulfur (E. Merck GmbH) were used without further purification. SCl_2 and S_2Cl_2 (Fluka Chemie AG) were distilled over PCl_3 in a nitrogen atmosphere. Se_2Cl_2 was prepared as described by Fehér.[22] $[(Me_3Si)_2N]_2S$ was prepared from $(Me_3Si)_2NH$ by utilizing the method of Wolmershäuser *et al.*[12c] The solvents were dried by freshly distilling under a nitrogen atmosphere: dichloromethane (E. Merck GmbH) and carbon disulfide (E. Merck GmbH) over P_4O_{10}, and diethyl ether (E. Merck GmbH) over Na/benzophenone.

Caution! *The six-membered $Se_xS_{4-x}N_2$ ring molecules may be explosive under the influence of heat or mechanical stress, especially with higher selenium contents when the possibility of the formation of $Se_3N_2Cl_2$ is increased. The reaction products should be stored and handled under hydrocarbon solvents and their preparation limited to amounts of <1.0 g.*

Preparation of S_4N_2. $[(Me_3Si)_2N]_2S$ (0.352 g, 1 mmol) was dissolved in 10 mL of dichloromethane, and a mixture of 0.102 g (1 mmol) of SCl_2 and 0.134 g (1 mmol) of S_2Cl_2 in 10 mL of dichloromethane was added dropwise at −78 °C. The reaction mixture was allowed to warm slowly to room temperature with stirring for 12 h and was found to contain 80% of S_4N_2 and 20% of S_4N_4 as judged by the ^{14}N NMR spectrum of the reaction mixture.[23] After the red solution was filtered and the solvent removed by evaporation, a dark red tar was formed. The crude product was sublimed at room temperature (<10 Pa). Subsequent recrystallization from diethyl ether yielded 0.101 g [65% based on the initial amount of $[(Me_3Si)_2N]_2S$] of

---

(11) Chivers, T.; Laitinen, R. S.; Maaninen, A.; Pyykkönen, S.; Siivari, J. *Univ. of Oulu Rep. Ser. Chem.* **1993**, *42*, P18.

(12) (a) Haas, A.; Kasprowski, J.; Angermund, K.; Betz, P.; Krüger, C.; Tsay, Y.-H.; Werner, S. *Chem. Ber.* **1991**, *124*, 1895. (b) Haas, A.; Kasprowski, J.; Pryka, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1144. (c) Wolmerhäuser, G.; Brulet, C. R.; Street, G. B. *Inorg. Chem.* **1978**, *17*, 3586.

(13) (a) Siivari, J.; Laitinen, R. S.; Hiltunen, Y. *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *65*, 177. (b) Siivari, J.; Chivers, T.; Laitinen, R. S. 75th Canadian Chemical Conference and Exhibition, Edmonton, 1992; 336 IN-D5P.

(14) The preliminary results of this work have been presented in the 7th International Symposium on Inorganic Ring Systems held in Banff, Canada, on August 7−12, 1994, and have been presented in the conference proceedings.[15]

(15) Siivari, J.; Suontamo, R. J.; Laitinen, R. S.; Chivers, T. *Phosphorus Sulfur Silicon Relat. Elem* **1994**, *93/94*, 245.

(16) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A., *Gaussian 92,* Revision A Gaussian, Inc., Pittsburgh PA, 1992.

(17) Sakai, Y.; Tatewaki, H.; Huzinaga, S., *J. Comput. Chem.* **1982**, *3*, 6.

(18) The need for *d*-polarization functions for the correct geometry prediction of chalcogen−chalcogen bonds is well established (see, for instance, ref 19)

(19) Hinchliffe, A. *J. Mol. Struct.* **1979**, *55*, 127.

(20) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229. (c) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *10*, 1.

(21) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, *15*, 269.

(22) Fehér, F. In *Handbuch der präparativen Anorganischen Chemie*, 3rd ed.; Brauer, G., Ed.; Ferdinand Enke Verlag: Stuttgart, 1975, Vol. 1, p 415.

(23) ^{14}N NMR: (a) −112 ppm (S_4N_2); (b) −256 ppm (S_4N_4).[24]

Table 1. Optimized Bond Parameters of $Se_xS_{4-x}N_2$ ($x = 0-4$)[a]

	A												
parameter[b]	calc	exptl[c]	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**
r_1 (pm)	208.5	206.1	208.6	221.2	208.7	221.3	221.4	208.6	221.4	233.9	221.4	221.7	234.0
r_2 (pm)	208.5	206.1	221.3	221.2	208.7	221.3	233.6	221.7	221.4	233.9	221.4	233.9	234.0
r_3 (pm)	171.8	167.5	171.7	171.8	171.0	184.9	171.8	170.7	171.1	185.1	184.1	170.8	184.2
r_4 (pm)	171.8	167.5	185.1	171.8	171.0	184.9	185.2	184.3	171.1	185.1	184.1	184.4	184.2
r_5 (pm)	154.8	156.1	154.8	154.8	168.6	154.4	154.8	168.5	168.6	154.3	168.0	168.6	168.0
r_6 (pm)	154.8	156.1	154.4	154.8	168.6	154.4	154.3	168.2	168.6	154.3	168.0	168.1	168.0
α_1 (deg)	99.8	102.9	99.7	96.0	101.4	99.6	96.0	101.4	97.6	95.9	101.2	97.6	97.6
α_2 (deg)	102.9	103.4	104.1	102.9	104.2	101.1	104.0	105.3	104.2	101.1	102.1	105.1	102.1
α_3 (deg)	102.9	103.4	99.6	102.9	104.2	101.1	99.7	100.8	104.2	101.1	102.1	100.9	102.1
α_4 (deg)	125.8	126.7	127.1	126.9	124.8	127.4	128.0	126.8	125.8	128.4	126.4	127.5	127.4
α_5 (deg)	125.8	126.7	126.1	126.9	124.8	127.4	127.3	124.4	125.8	128.4	126.4	126.7	127.4
α_6 (deg)	123.6	122.9	124.3	124.4	120.3	125.0	125.1	121.2	121.2	125.6	122.0	122.1	122.8
τ_1 (deg)	−60.9	−57.5	−61.7	−60.0	−63.0	−59.6	−61.1	−62.7	−62.1	−58.9	−61.8	−62.4	−61.0
τ_2 (deg)	60.9	57.5	59.2	60.0	63.0	59.6	58.1	62.2	62.1	58.9	61.8	60.8	61.0
τ_3 (deg)	37.3	34.9	38.6	38.8	37.6	37.1	40.5	36.9	39.2	38.6	37.2	39.5	38.7
τ_4 (deg)	−37.3	−34.9	−35.9	−38.8	−37.6	−37.1	−37.0	−38.0	−39.2	−38.6	−37.2	−38.5	−38.7
τ_5 (deg)	−5.7	−5.9	−5.5	−6.0	−6.1	−5.6	−6.2	−5.0	−6.7	−6.0	−5.9	−6.1	−6.4
τ_6 (deg)	5.7	5.9	5.7	6.0	6.1	5.6	5.8	7.4	6.7	6.0	5.9	7.2	6.4

[a] For the identification of the different isomers, see Figure 1. [b] *r* is the bond length, a the bond angle, and t the torsional angle (+ clockwise, − anticlockwise). For the numbering of atoms and bonds, see Figure 2. [c] See ref 5b.

S_4N_2 as dark red crystals (The ^{14}N NMR spectrum showed only one resonance at −112 ppm[24]).[25]

Preparation of SeS_3N_2. The treatment of 10 mL of a CH_2Cl_2 solution of $[(Me_3Si)_2N]_2S$ (0.408 g, 1.12 mmol) with 10 mL of a CH_2Cl_2 solution containing 0.090 mL (1.12 mmol) of S_2Cl_2, 0.082 g (0.37 mmol) of $SeCl_4$, and 0.085 g (0.37 mmol) of Se_2Cl_2 at −78 °C afforded a dark red insoluble precipitate. The elemental analysis and ^{77}Se NMR spectrum imply that the product contains 92% of SeS_3N_2 and 8% of Se.[26] The yield was 0.210 g [85% based on the initial amount of $[(Me_3Si)_2N]_2S$ and assuming the product to be a mixture of SeS_3N_2 and Se]. The identification of the SeS_3N_2 is discussed in the Results and Discussion section.

Spectroscopy and Vibrational Analysis. The ^{14}N and the ^{77}Se NMR spectra were recorded on a Bruker DPX 400 spectrometer at 300 K operating at 28.911 and 76.410 MHz for ^{14}N and ^{77}Se, respectively. The spectral widths were 10.42 and 114.94 kHz, yielding the respective resolutions of 1.24 and 1.75 Hz/data point. The ^{14}N pulse width was 5.70 μs, and that for ^{77}Se 6.70 μs, corresponding to nuclear tip angles of 21 and 46°, respectively. The ^{14}N accumulations contained 40 960 transients, and the ^{77}Se accumulations 40 000 transients. D_2O was used as an external ^2H lock and CH_3NO_2 and the saturated solution of SeO_2 were used as external references. The ^{14}N chemical shifts were reported relative to the external reference, and the ^{77}Se chemical shifts relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$].

MS-EI mass spectra were recorded by using a Kratos MS 80 spectrometer at 12 eV of electron energy. The IR spectra were recorded as Nujol mulls by using a Bruker IFS-66 spectrometer. The same instrument equipped with a FRA-16 Raman unit and a Nd:YAG laser was utilized to obtain the low-temperature (∼−100 °C) Raman spectra of all products directly from solid samples.

Fundamental vibrations were calculated for S_4N_2 and for the different isomers of SeS_3N_2 by using a general valence force field approach.[27] The **F**-matrix of S_4N_2 contained seven diagonal force constants and one off-diagonal interaction force constant (adjacent SS/SS bond−bond interaction). Analogous force fields of the isomers **B**−**D** (see Figure 1) contained 10−12 force constants. The molecular geometries of all isomers were estimated on the basis of the optimized bond parameters obtained from the *ab initio* calculations (see Table 1). The initial values of the force constants were estimated from those of the related molecules.[28−31]

The force constants of S_4N_2 were refined simultaneously by adjusting the observed nine IR bands[5b] to the calculated values until no further change was observed. In the case of SeS_3N_2, the adjustment of the observed Raman lines was attempted for all three isomers. The calculated HF/MIDI-4* frequencies of Table 2 were used as guidelines for the initial assignment of the observed spectrum. Only in the case of isomer **C** were the observed and calculated fundamental vibrations in mutual agreement *and* the refined diagonal force constants assumed positive values.

Results and Discussion

Geometries and Relative Stabilities of $Se_xS_{4-x}N_2$ ($x = 0-4$). The MIDI-4* optimized molecular geometries of all 12 possible $Se_xS_{4-x}N_2$ isomers are shown in Table 1. All molecules are remarkably similar and exhibit an optimum geometry with an approximate half-chair conformation that is well established experimentally for S_4N_2.[5] It can be seen from Table 1 that the calculated bond parameters of S_4N_2 are in good agreement with the experimental data. While there is no experimental information for other $Se_xS_{4-x}N_2$ species, their calculated bond parameters are reasonable when compared to those of S_4N_2. The chalcogen−chalcogen bonds in the NEEEN fragments (E = S, Se) show parameters expected for single bonds. The nitrogen−chalcogen bond lengths in this fragment also approach those of

---

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

(25) The preparation of $[(Me_3Si)_2N]_2S$ from $(Me_3Si)_2NH$ and *n*-BuLi proceeds via the formation of $(Me_3Si)_2NLi$.[12c] S_4N_2 was also prepared directly by treating 1.88 g (20 mmol) of $(Me_3Si)_2NLi$ dissolved in 10 mL of CH_2Cl_2 with a mixture of 2.04 g (20 mmol) of SCl_2 and 1.34 g (10 mmol) of S_2Cl_2 dissolved in 10 mL of CH_2Cl_2 at −78 °C. The solution was allowed to warm slowly to room temperature. After filtration of the orange solution and subsequent sublimation and recrystallization from diethyl ether, 0.88 g [56% yield based on the initial amount of $(Me_3Si)_2NH$] of S_4N_2 was obtained as dark red crystals.

(26) Anal. Calcd for SeS_3N_2: N, 13.8; S, 47.3; Se, 38.9. Found: N, 13.2; S, 43.2; Se, 43.6. On basis of the ^{77}Se NMR spectrum, the excess selenium was assumed to be elemental selenium. This led to a product distribution of 92.3% of SeS_3N_2 and 7.7% of Se. Anal. Calcd for this mixture: N, 12.7; S, 43.6; Se, 43.6.

(27) McIntosh, D. F.; Peterson, M. R. General Vibrational Analysis Programs Utilizing the Wilson GF Matrix Method for a General Unsymmetrized Molecule. *QCPE*, **1977**, 342.

(28) Steudel, R.; Mäusle, H.-J. *Z. Naturforsch., A* **1978**, *33*, 951.

(29) Laitinen, R.; Rautenberg, N.; Steidel, J.; Steudel, R. *Z. Anorg. Allg. Chem.* **1982**, *486*, 116.

(30) (a) Steudel, R. *Z. Naturforsch., A* **1981**, *36*, 850. (b) Steudel, R. *J. Phys. Chem.* **1977**, *81*, 343. (c) Steudel, R.; Rose, F. *Spectrochim. Acta* **1977**, *33A*, 979. (d) Steudel, R.; Steidel, J.; Rautenberg, N. *Z. Naturforsch.*, **1980**, *35*, 792.

(31) Brooks, W. V. F.; Cameron, S. T.; Parsons, S.; Passmore, J.; Schriver, M. J. *Inorg. Chem.* **1995**, *33*, 6230.

Table 2. Fundamental Vibrations of the $Se_xS_{4-x}N_2$ ($x = 0-4$) Isomers (in cm^{-1})

S_4N_2[a]	SeS_3N_2[a]			$Se_2S_2N_2$[a]				Se_3SN_2[a]			Se_4N_2 **L**	
A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	MIDI-4*	3-21G*[b]
1113 a″	1112	1114 a″		1110 a″	1112			1110 a″				
1011 a′	1016	1011 a′		1020 a′	1016			1021 a′				
			937 a″			932	937 a″		922 a″	931	921 a″	951 a″
			895 a′			893	893 a′		901 a′	895	901 a′	939 a′
647 a′	632	637 a′			624							
628 a″				608 a′		593	602 a′	599 a′				
	592	626 a″	612 a′		587					585	548 a′	509 a′
			582 a″				577 a″					
545 a′		538 a′		534 a″		537		529 a″	556 a′	530		
482 a′	479								500 a″		495 a″	
464 a″	470		473 a′		471	464						458 a″
			452 a″	432 a′			430 a′	428 a′				
		407 a′	436 a′		389					394		
	381			381 a″		393			376 a″			
364 a′		370 a″		380 a′		371	383 a′		374 a′			
	352	346 a′					359 a″			358		
306 a″				337 a′	338			334 a′	328 a′		321 a′	326 a′
			295 a′									
	271	281 a″	286 a″		275	281	280 a′	276 a′		274	277 a′	277 a″
262 a′							264 a″	268 a″	266 a′	265	264 a″	258 a′
				234 a″	252	239		224 a″		226	256 a′	258 a′
	215	211 a′	233 a′	183 a′	180	197	191 a′		210 a″		202 a″	212 a″
171 a′	151		150 a′					151 a′	164 a′	165		
		137 a′				136					137 a′	138 a′
134 a″		135 a″		125 a′	125		117 a′					
	118		110 a″	109 a″	115		115 a″	111 a″	117 a′	105		107 a″
						98		99 a′	91 a″	101	95 a″	
											89 a′	85 a′

[a] MIDI-4*. [b] Reference 6.

single bonds.[32] The bonds in the NEN units, on the other hand, are clearly shorter, indicating double bond character. Chivers *et al.*[5b] compared the electronic structure of S_4N_2 with that of the planar $S_3N_3^-$ ion. Their *ab initio* Hartree−Fock−Slater calculations indicate that while the planar conformation of S_4N_2 shows significant net π-bonding in the NSN fragment there is virtually no net π-bonding in the bonds of the NSSSN unit. In the half-chair conformation the σ-system in the S_3 and NSN fragments is strengthened with weakening of the central N−S bonds (bonds 3 and 4; see Figure 2). The net effect favors a nonplanar geometry. The calculated HF/MIDI-4* fundamental vibrations shown in Table 2 indicate that all molecules lie in the true local energy minima.

The energies of the valence orbitals of all $Se_xS_{4-x}N_2$ molecules are rather similar. The bonding in the NEEEN units is rather insensitive to the nature of the chalcogen atoms in the fragment. A similar effect had previously been demonstrated for trichalcogen hydrides and indicates the similarity of the SS, SeS, and SeSe bonds.[35] The energies of the orbitals describing the bonding in the NEN unit depend, however, on the nature of the chalcogen atom between the two nitrogen atoms. The molecular orbitals describing the bonding in the NSN unit (isomers **A**−**C**, **E**, **F**, **I**) lie systematically somewhat lower in energy than those of a NSeN unit (isomers **D**, **G**, **H**, **J**−**L**).

The total energies of the 12 molecules are shown in Table 3.

Table 3. MP2/MDI-4* Total Energies and Binding Energies of $Se_xS_{4-x}N_2$ ($x = 0-4$) ring molecules (in au)

species[a]		total energy		
		HF/MIDI-4*	MP2/MIDI-4*	ZPE[b]
S_4N_2	**A**	−1696.947 66	−1697.817 06	0.015 68
SeS_3N_2	**B**	−3697.544 69	−3698.410 42	0.014 82
	C	−3697.544 82	−3698.410 40	0.014 88
	D	−3697.516 80	−3698.401 53	0.013 98
$Se_2S_2N_2$	**E**	−5698.142 26	−5699.004 27	0.013 96
	F	−5698.143 19	−5699.004 50	0.014 04
	G	−5698.113 62	−5698.994 63	0.013 14
	H	−5698.114 05	−5698.995 14	0.013 18
Se_3SN_2	**I**	−7698.742 05	−7699.599 10	0.013 19
	J	−7698.710 84	−7699.587 74	0.012 30
	K	−7698.712 16	−7699.588 89	0.012 36
Se_4N_2	**L**	−9699.310 69	−9700.182 85	0.011 54

[a] For the identification of the different isomers, see Figure 1. [b] The zero point energies have been multiplied by 0.89.[21]

All molecules are stable relative to free atoms. The total binding energy of each isomer is shown in Figure 3a.[36] It can be seen that the total binding energy diminishes as the selenium content of the molecule increases. Within a given composition, isomers containing a NSeN unit show less binding than those containing a NSN unit. From the energy values given in Table 3 it can be

---

(32) Pauling[33] estimated the following single bond lengths: S−S 208 pm, Se−S 221 pm, Se−Se 234 pm, S−N 174 pm, and Se−N 186 pm. These values are in agreement with those observed experimentally as exemplified by the following compounds: S−S 205.5 pm (orthorhombic α-S_8),[34a,b] Se−S 218.5 pm [central Se−S bond of $[(O_3S)_2SSe]^{2-}$ in $K_2SeS_3O_6{\cdot}H_2O$],[34c] Se−Se 235.0 pm (monoclinic α-Se_8),[34d] S−N 171.6 pm $[(Me_3Si)_2NSN(SiMe_3)_2]$,[34e] Se−N 186.9 pm $[(Me_3Si)_2NSeN(SiMe_3)_2]$,[34f] S=N 153.6 pm $[(Me_3Si)NSN(SiMe_3)]$,[34g] and Se=N 171.0 pm $[[SnCl_4{\cdot}(^tBuN)_2Se]{\cdot}2thf]$.[34h]

(33) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7.

(34) (a) Coppens, P.; Yang, Y. W.; Blessing, R. H.; Cooper, W. F.; Larsen, F. K. *J. Am. Chem. Soc.* **1977**, *99*, 760. (b) Rettig, S. J.; Trotter, J. *Acta Crystallogr., Sect. C* **1987**, *43*, 2260. (c) Foust, A. S.; Janickis, V.; Marfy, K. *Inorg. Chem.* **1980**, *19*, 1040. (d) Cherin, P.; Unger, P. *Acta Crystallogr., Sect. B* **1972**, *28*, 313. (e) Schubert, G.; Kiel, G.; Gattow, G. *Z. Anorg. Allg. Chem.* **1989**, *575*, 129. (f) Björgvinsson, M.; Roesky, H. W.; Pauer, F.; Stalke, D.; Sheldrick, G. M. *Inorg. Chem.* **1990**, *29*, 5140. (g) Anderson, D. G.; Robertson, H. E.; Rankin, D. W. H.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 859. (h) Gindl, J.; Björgvinsson, M.; Roesky, H. W.; Freie-Erdbrügger, C.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1993**, 811.

(35) Laitinen, R.; Pakkanen, T. *J. Mol. Struct. (THEOCHEM)* **1983**, *91*, 337.

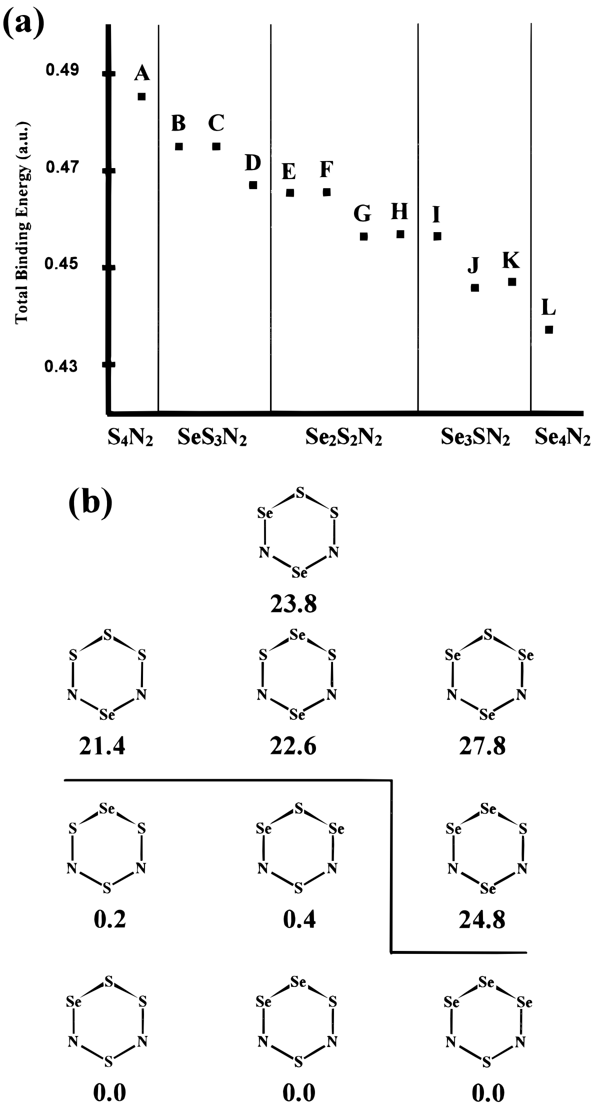


Figure 3. (a) Total binding energies (in au) of $Se_xS_{4-x}N_2$ ($x = 0-4$). For the identification of the different isomers, see Figure 1. (b) Relative energies (in kJ mol^{-1}) of all isomers of SeS_3N_2 (**B**−**D**), $Se_2S_2N_2$ (**E**−**H**), and Se_3SN_2 (**I**−**K**)

seen that the NSeN unit is ~25 kJ mol^{-1} less stable than the NSN unit (see Figure 3b).[37] The selenium atoms are therefore preferably located in the NEEEN unit (E = S, Se). The relative energies of the isomers seem to be virtually independent of the distribution of sulfur and selenium atoms within this fragment.

Preparation and Characterization of S_4N_2. Tetrasulfur dinitride can conveniently be prepared in good yield by the reaction of $[(Me_3Si)_2N]_2S$ with SCl_2 and S_2Cl_2 in CH_2Cl_2:

$$[(Me_3Si)_2N]_2S + SCl_2 + S_2Cl_2 \rightarrow S_4N_2 + 4Me_3SiCl \quad (1)$$

In addition to S_4N_2, the reaction solution was found to contain some S_4N_4 as judged by ^{14}N NMR spectroscopy. The ^1H NMR spectrum of the solution indicated that Me_3SiCl (δ = 0.40 ppm[39]) is the exclusively formed byproduct in this reaction. Purification by sublimation and recrystallization from diethyl ether[5b] yielded dark red crystals of low melting point that were identified as S_4N_2 by ^{14}N NMR spectroscopy[23a] and IR spectroscopy.

Vibrational analysis using the general valence force field approach with eight force constants provided a good agreement between the observed and calculated fundamental vibrations as shown in Table 4. The main contributions in the calculated potential energy distribution are also shown in Table 4 and enable the assignment of the observed IR bands. Expectedly, the two bands at 1034 and 918 cm^{-1} are mainly the asymmetric and symmetric $\nu_{S=N}$ stretching modes though the latter is coupled with the ν_{S-N} stretching vibrations. The main asymmetric and symmetric ν_{S-N} stretching modes are represented by the two bands at 628 and 561 cm^{-1}, respectively. The symmetric and asymmetric S−S stretching vibrations are found at 635 and 376 cm^{-1}, respectively. The bending and torsion modes lie generally at smaller wavenumbers with the exception of a band at 469 cm^{-1} that is almost exclusively due to torsional vibrations. This assignment is in contrast with that presented earlier by Chivers *et al.*,[5b] who discussed the origin of the two signals at 561 and 469 cm^{-1}. Isotopic substitution with ^{15}N caused virtually no isotope shift, and it was therefore thought possible that these bands are due to the asymmetric and symmetric ν_{S-S} stretching modes, respectively. The disappearance of the band at 561 cm^{-1} upon dissolution, however, seemed to contradict this conclusion. Their conclusion that S_4N_2 is a strongly coupled system is confirmed by the potential energy distribution of Table 4.

The vibrational analysis yielded reasonable force constants for S_4N_2. The stretching force constants are compared with those of related species in Table 5.

Preparation and Characterization of SeS_3N_2. The introduction of a selenium atom into the six-membered ring was attempted by the reaction of $[(Me_3Si)_2N]_2S$ with a mixture of sulfur and selenium chlorides. The molar ratio of sulfur to selenium was adjusted to 3:1 and that of chalcogen to nitrogen was kept constant at 2:1 (*cf.* the preparation of S_4N_2):

$$3[(Me_3Si)_2N]_2S + 3S_2Cl_2 + Se_2Cl_2 + SeCl_4 \rightarrow 3SeS_3N_2 + 12Me_3SiCl \quad (2)$$

The resulting dark brown-red material was almost insoluble in organic solvents and precipitated during the reaction.[40] It was separated from the reaction mixture by filtration and washed several times with CH_2Cl_2. The purified material was then extracted with CH_2Cl_2, and the ^{77}Se NMR spectrum was recorded from the resulting solution.[43] The spectrum showed

---

(36) The MP2/MIDI-4* total energies of the free atoms are the following (in au): N −54.365 81, S −397.146 51, Se −2397.750 91. These values lead to the following total energies for the five possible elemental compositions, assuming that no bonds are formed: S_4N_2 −1697.317 66, SeS_3N_2 −3697.922 06, $Se_2S_2N_2$ −5698.526 46, Se_3SN_2 −7699.130 86, and Se_4N_2 −9699.735 26.

(37) Indirect experimental support comes from the observation that whereas the silylated sulfur diimide $Me_3SiNSNSiMe_3$ is stable,[2] the selenium analogue, $Me_3SiNSeNSiMe_3$ is not.[38]

(38) Fockenberg, F.; Haas, A. *Z. Naturforsch.* **1986**, *41B*, 413.

(39) Pouchert, C., Ed. *The Aldrich Library of NMR Spectra*, 2nd ed.; Aldrich: Milwaukee, WI, 1983; Vol. 2, p 995A.

(40) The ^{14}N NMR spectrum of the initial CH_2Cl_2 solution over the crude reaction mixture showed several resonances at −46, −57, −112, −121, and −256 ppm. The resonance at −112 ppm is due to S_4N_2 [23a] and that at −256 ppm is due to S_4N_4.[23b] The resonance at −57 is assigned to $Me_3SiN{=}S{=}NSiMe_3$ that can be shown to be produced as a single product from the reaction of $[(Me_3Si)_2N]_2S$ with an equimolar amount of SO_2Cl_2.[41] According to Parkin *et al.*,[42] $S_3N_2Cl_2$ exhibits two signals at −55 and −125 ppm. Our resonances at −57 and −121 ppm can therefore be assigned to this species. The resonance at −46 ppm is due to an unknown species that is removed during the purification of the product by distillation, and is therefore unlikely to contain selenium.

(41) The identity of $Me_3SiN{=}S{=}NSiMe_3$ was verified by treating the product with an equimolar amount of SCl_2 whereupon S_4N_4 was produced.

(42) Parkin, J. P.; Woollins, J. D.; Belton, P. S. *J. Chem. Soc., Dalton Trans.* **1990**, 511.

(43) We did not observe a single ^{14}N NMR resonance in the spectrum of the CH_2Cl_2 or CS_2 solution of the recrystallized product.

Table 4. Calculated and Observed Fundamental Vibrations (cm^{-1}) of S_4N_2 (**A**) and the Main Contributions in the Calculated Potential Energy Distribution (%) along the Internal Coordinates[a]

		stretching modes						bending modes						
calc	obs[b]	r_1 $_{S-S}$	r_2 ν_{S-S}	r_3 ν_{S-N}	r_4 ν_{S-N}	r_5 ν_{S-N}	r_6 $\nu_{S=N}$	α_1 δ_{S-S-S}	α_2 δ_{S-S-N}	α_3 δ_{S-S-N}	α_4 $\delta_{S-N=S}$	α_5 $\delta_{S-N=S}$	α_6 $\delta_{S=N=S}$	torsion modes[c]
1034 a″	1034 s					45	45							
918 a′	918 w			15	15	35	35							
635 a′	635 s	30	30											
628 a″	628 vs			40	40									
562 a′	561 m			20	20									10
467 a′	469 m													90
376 a″	376 ms	45	45											
321 a′	322 m										25	25	10	
273 a″	266 vw													90
232 a″											25	25		
159 a′									15	15				65
147 a′								50	10	10			12	

[a] For the definition of atoms and bonds, see Figure 2. The potential energy contributions have been rounded to the nearest 5%. Minor contributions of <10% are not shown. [b] The observed wavenumbers have been taken from the IR spectrum, see ref 5b. [c] All contributions to the potential energy distribution from the torsion modes have been summed together and are shown if the sum exceeds 10%.

Table 5. Comparison of Selected Stretching Force Constants of S_4N_2 and SeS_3N_2 with Some Related Species (N m^{-1})

force const	S_4N_2 (**A**)[a]	SeS_3N_2 (**C**)[a]	S_8[b]	Se_3S_5[c]	S_4N_4[d]	S_7NH[e]	$S_4(NH)_4$[f]	$S_3N_2O_2$[g]	$SNSNS^{2+}$[h]	$SeNSNSe^{2+}$[h]
f_{S-S}	280		241	221–227		223–253			155[i]	
f_{Se-S}		155		196						
f_{S-N}	249	286			376	398	401	220	333[j]	339[j]
$f_{S=N}$	476	424						550	443[k]	
f_{Se-N}										425

[a] This work. [b] Reference 28. [c] Reference 29. [d] Reference 30a. [e] Reference 30b. [f] Reference 30c. [g] Urey–Bradley force constants.[30d] [h] Reference 31. [i] The estimated bond order is 0.8. [j] The estimated bond order is 1.6–1.7. [k] The estimated bond order is 1.95.

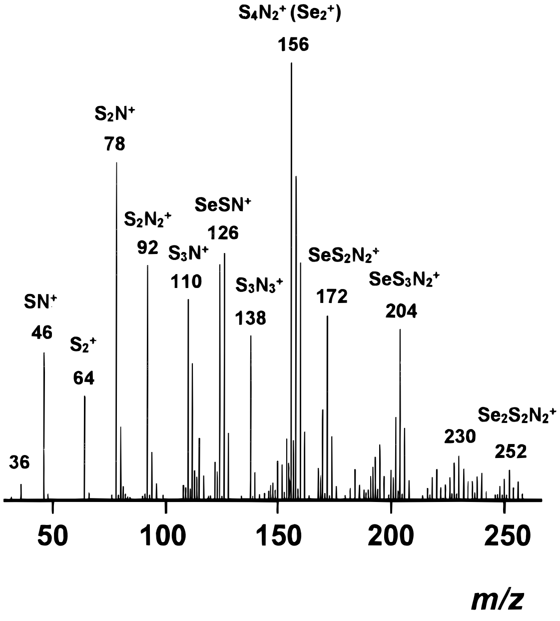


Figure 4. The 12 eV mass spectrum of SeS_3N_2.

Table 6. Calculated and Observed Isotopic Distribution (%) of SeS_3N_2 and $Se_2S_2N_2$ (see Figure 4)

SeS_3N_2			$Se_2S_2N_2$		
m/e	I_{obs}	I_{calc}	m/e	I_{obs}	I_{calc}
198	3.3	1.7	246	17.2	18.6
200	17.4	17.2	247	10.3	12.2
201	14.0	14.8	248	48.3	48.6
202	47.9	47.1	249	24.1	26.2
203	5.0	3.4	250	84.5	84.6
204	100.0	100.0	251	8.6	8.5
205	4.1	3.2	252	100.0	100.0
206	38.0	30.2	253	4.1	2.7
207	0.8	0.8	254	46.6	37.6
208	9.9	2.9	255		0.8
			256	a	5.5

[a] Obscured by S_8^+ ion.

initially two resonances at 780 and 622 ppm with the former more intense than the latter. With longer accumulation the resonance at 780 ppm started to disappear, that at 622 ppm became stronger, and new resonances appeared at 660 and 560 ppm. These two latter resonances showed a constant intensity ratio of 2:1. The assignment of these resonances is discussed below.

The elemental analysis of the solid product from reaction 2 can be inferred in terms of a mixture containing 92% of SeS_3N_2 and 8% of Se.[26] The 12 eV mass spectrum shown in Figure 4 indicates the presence of SeS_3N_2 in the sample with small amounts of $Se_2S_2N_2$. The observed and calculated isotopic distributions are in excellent agreement with each other for both molecular ions (see Table 6). The fragmentation pattern shown in Figure 4 is for most part consistent with the molecular composition of SeS_3N_2. Only the signals due to $S_4N_2^+$ (overlapped with Se_2^+) and to $S_3N_3^+$ are not easily interpreted in terms of the fragmentation of SeS_3N_2 or $Se_2S_2N_2$. As discussed above, some S_4N_2 was found in the initial filtrate. After recrystallization, however, no traces of S_4N_2 were observed in the ^{14}N NMR spectrum of the final CH_2Cl_2 solution.[44] In any case, SeS_3N_2 seems to be the main component of the brown-red material.

There are three isomers of SeS_3N_2 (see Figure 1). The *ab initio* study described above indicates that the NSN unit is more stable than the NSeN unit in these compounds (see Figure 3b). This favors isomers **B** and **C** over isomer **D**. The formation of

---

(44) It is possible that S_4N_2 and $Se_xS_{4-x}N_2$ form solid solutions and thus S_4N_2 is prevented from dissolution by occlusion. The two Raman and IR bands at 625 and 469 cm^{-1} (see Figure 5 and footnote 45) that cannot be assigned in terms of isomer **C** may well be due to S_4N_2 (see Table 4). The elemental analysis of the product, however, allows only negligible amounts of S_4N_2 to be present in the phase.[26]

Table 7. Calculated and Observed Fundamental Vibrations (cm^{-1}) of SeS_3N_2 (**C**) and the Main Contributions in the Calculated Potential Energy Distribution (%) along the Internal Coordinates[a]

		stretching modes						bending modes						
calc	obs[b]	r_1 ν_{Se-S}	r_2 ν_{Se-S}	r_3 ν_{S-N}	r_4 ν_{S-N}	r_5 $\nu_{S=N}$	r_6 $\nu_{S=N}$	α_1 δ_{S-Se-S}	α_2 δ_{Se-S-N}	α_3 δ_{Se-S-N}	α_4 $\delta_{S-N=S}$	α_5 $\delta_{S-N=S}$	α_6 $\delta_{S=N=S}$	tors[c]
976 a″	973 m			15	15	35	35							
957 a′	960 m			20	20	25	25							
723 a′	723 m													100
581 a″	575 w			20	20	20	20							
518 a′	531 s			10	10	25	25							
417 a′	408 s			10	10						20	20	20	
384 a″	378 m	20	20						10	10				30
359 a′	359 m	40	40										10	
312 a″	312 vs	10	10											55
252 a″	271 w	20	20								20	20		
148 a′	162 vs								25	25				40
128a′	129 vs							20					20	35

[a] For the definition of atoms and bonds, see Figure 2. The potential energy contributions have been rounded to the nearest 5%. Minor contributions of <10% are not shown. [b] For the Raman spectrum, see Figure 5. [c] All contributions to the potential energy distribution from the torsion modes have been summed together and are shown if the sum exceeds 10%.

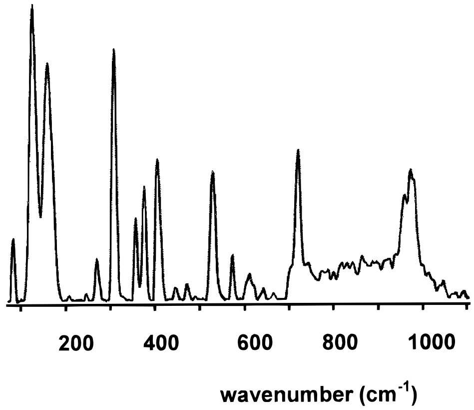


Figure 5. Raman spectrum of SeS_3N_2 recorded at ∼−100 °C.

these two former isomers is also consistent with the synthetic route that was used (eq 2).

The Raman spectrum of the product is shown in Figure 5.[45] The fundamental vibrations calculated for SeS_3N_2 (isomer **C**) by using the valence force field approach described above for S_4N_2 yielded a good agreement with the observed Raman lines as shown in Table 7. The assignment based on the calculated potential energy distribution is reasonable when compared to that of S_4N_2 (see Table 4). It can be seen that several normal modes contribute to a given fundamental vibration. The refined force constants are reasonable, as exemplified by the stretching force constants in Table 5. It seems that the main component of the reaction 2 is indeed the isomer **C** of SeS_3N_2 with the selenium atom in the central position of the fragment NEEEN (see Figure 1).

The Raman spectrum, however, does not rule out the presence of minor components of the mixture, since their detection limits would be expected to be of the order of 10%. There are some weak unassigned lines in the Raman spectrum (see Figure 5) that also appear in the IR spectrum.[45] Those at 625 and 469 cm^{-1} may well be due to small amounts of S_4N_2 in the product, though the former could also be an overtone of the very strong band at 312 cm^{-1} and the latter a combination vibration of the Raman lines at 312 and 169 cm^{-1}. The appearance of the bands at 625 and 469 cm^{-1} also in the IR spectrum, however, renders their assignment to S_4N_2 more likely than as combination vibrations. The Raman line at 440 cm^{-1} is likely to be the combination vibration of the two very strong Raman lines at 312 and 129 cm^{-1}.

The ^{77}Se NMR resonance can be assigned in terms of isomer **C**. The ^{77}Se chemical shift of 780 ppm is typical for selenium surrounded by two sulfur atoms as deduced previously for heterocyclic Se_nS_{8-n} species.[46] The second resonance at 622 ppm observed initially in the spectrum is due to Se_8.[46] With longer accumulation, the sample decomposes as evidenced by the lowering of the intensity of the resonance at 780 ppm, by the increase of the Se_8 resonance at 622 ppm, and by the appearance of two new resonances at 660 and 560 ppm with a constant respective intensity ratio of 2:1. The last two resonances can be assigned to 1,2,3-Se_3S_5.[46] At the same time, the formation of a dark red precipitate is observed in the NMR tube.

The formation of isomer **C** in reaction 2 requires the rupture of both the S−S bond in S_2Cl_2 and the Se−Se bond in Se_2Cl_2. It has, however, been deduced earlier that in solution the two dichalcogen chlorides are in equilibrium with $SeSCl_2$.[47] This and other appropriate equilibria between the different chalcogen chlorides in the solution may explain the origin of the NSSeSN fragment in the final product.

Attempted Preparations of $Se_xS_{4-x}N_2$ (x = 2, 3). Attempts were made to introduce more than one selenium atom into the six-membered chalcogen−nitrogen ring by increasing the relative content of selenium in the chalcogen chloride mixture (see eqs 3 and 4).

$$[(Me_3Si)_2N]_2S + SCl_2 + Se_2Cl_2 \rightarrow Se_2S_2N_2 + 4Me_3SiCl \qquad (3)$$

$$3[(Me_3Si)_2N]_2S + 4Se_2Cl_2 + SeCl_4 \rightarrow 3Se_3SN_2 + 12Me_3SiCl \qquad (4)$$

Both reactions resulted in the formation of dark brown-red insoluble solids with Me_3SiCl as the sole byproduct. The 12 eV mass spectrum of the product of reaction 3 indicated the formation of $Se_2S_2N_2$ in addition to SeS_3N_2. The Raman spectrum of the product showed signals due to isomer **C**. In addition there were Raman lines at 461 (w), 354 (s), 259 (vs), and 108 cm^{-1} (m). The last two signals are most likely caused by elemental selenium.[48]

---

(45) The IR spectrum of the product shows absorption bands at 966, 939, 707, 575, 526, and 432 cm^{-1} in agreement with the Raman lines. In addition, there are absorption bands at 625 and 469 cm^{-1}.

(46) Laitinen, R. S.; Pakkanen, T. A. *Inorg. Chem.* **1985**, *26*, 2598.

(47) (a) Steudel, R.; Plinke, B.; Jensen, D.; Baumgart, F. *Polyhedron* **1991**, *10*, 1037. (b) Milne, J. B. *Can. J. Chem.* **1992**, *70*, 693.

The most prominent signals in the mass spectrum of the product from the reaction 4 were due to Se_n^+ fragments. In addition, very weak clusters due to Se_3SN_2, $Se_2S_2N_2$, and SeS_3N_2 could be observed. The Raman spectrum showed only lines due to elemental selenium.[48]

It must be concluded that reactions 3 and 4 produce only mixtures of $Se_xS_{4-x}N_2$ and elemental selenium. Especially, in the case of reaction 4 the desired products are formed only sparingly. This can be understood by taking into account the trend in the total binding energies as shown in Figure 3a. The stabilities of the six-membered chalcogen−nitrogen rings diminish with increasing selenium content. Thus it seems unlikely that Se_4N_2 is stable at room temperature. Consistently, attempts to prepare this selenium nitride by different methods have resulted in the formation of $Se_3N_2Cl_2$.[5,9]

Conclusions

$[(Me_3Si)_2N]_2S$ is a versatile reagent that reacts with chalcogen chlorides to yield a variety of heterocyclic chalcogen−nitrogen species, depending on the molar ratio of the starting materials. The reaction of $[(Me_3Si)_2N]_2S$ with equimolar amounts of SCl_2 and S_2Cl_2 produced S_4N_2 in a good yield. The reaction with S_2Cl_2, Se_2Cl_2, and $SeCl_4$ (molar ratio 3:1:1 in order to hold the chalcogen to chlorine ratio at 1:1 and the chalcogen to nitrogen ratio at 2:1) yielded a dark brown-red insoluble material that could be inferred to be essentially SeS_3N_2 (isomer **C**) on the basis of the elemental analysis, mass spectroscopy, vibrational analysis, and ^{14}N and ^{77}Se NMR spectroscopy. Attempts to prepare selenium-rich species resulted in the formation of elemental selenium or $Se_3N_2Cl_2$. These results are consistent with *ab initio* MO calculations which indicate that the relative stability of the different members of the series $Se_xS_{4-x}N_2$ ($x = 0-4$) reduces with increasing selenium content.

Acknowledgment. The financial support from the Academy of Finland and the Neste Oy Foundation is gratefully acknowledged.

IC9613570

---

[48] Steudel, R. *Z. Naturforsch.* **1975**, *30A*, 1481.