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Articles

Preparation, X-ray Structure, and Spectroscopic Characterization of 1,5-$Se_2S_2N_4$

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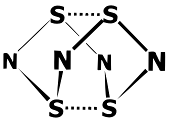
The reaction of $[(Me_3Si)_2N]_2S$ with equimolar amounts of SCl_2 and SO_2Cl_2 produces S_4N_4 in a good yield. The new chalcogen nitride 1,5-$Se_2S_2N_4$ has been prepared in high yield by two different reactions: (a) from $[(Me_3Si)_2N]_2S$ and $SeCl_4$ and (b) from $[(Me_3Si)_2N]_2Se$ with equimolar amounts of SCl_2 and SO_2Cl_2. 1,5-$Se_2S_2N_4$ has a cage structure similar to those of S_4N_4 and Se_4N_4. The crystal structure is disordered with site occupation factors ca. 50% for selenium in each chalcogen atom position. The 12 eV EI mass spectrum shows $Se_2SN_2^+$ as the fragment with highest mass. Both the ^{14}N and ^{77}Se NMR spectra show a single resonance (−238 and 1418 ppm, respectively). These data rule out the possibility that the crystalline sample is a solid solution of S_4N_4 and Se_4N_4 and imply the presence of 1,5-$Se_2S_2N_4$. This deduction was further verified by Raman spectroscopy and vibrational analysis.

Introduction

Tetrasulfur tetranitride S_4N_4 is a common starting material for the preparation of a wide variety of cyclic and acyclic sulfur−nitrogen species.[2] The crystal structure determinations [3] have established that the molecule exhibits a cage structure (**1**) with unusual bonding features that are still not completely understood.[4]



(**1**)

Two polymorphs are known for crystalline tetraselenium tetranitride Se_4N_4[6] one of them being isostructural with S_4N_4.[6b] In both polymorphic forms, however, the molecule shows a cage structure similar to S_4N_4. Though Se_4N_4 is extremely unstable and therefore difficult to handle in large amounts, it has proven to be a convenient source for both neutral and ionic Se−N species.[7]

The catalytic vapor phase decomposition of S_4N_4 produces cyclic S_2N_2 that polymerizes spontaneously to polymeric sulfur nitride $(SN)_x$.[11] It was discovered in 1970s that $(SN)_x$ has anisotropic semiconducting properties and that it becomes a superconductor below 0.33 K.[12] Other routes to produce polymeric sulfur nitride are also known.[13] The polymer $(SeN)_x$ and mixed chalcogen−nitrogen polymers are also expected to have interesting structural and electrical properties. Their preparation and characterization, however, have not been reported, probably because of the instability of the likely precursors.

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(1) (a) University of Oulu. (b) University of Calgary. (c) University of Joensuu.

(2) (a) Chivers, T. In *The Chemistry of Inorganic Homo- and Heterocycles;* Academic Press Inc.: London, 1987; Vol. 2, pp 793−869. (b) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, 36, 299.

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(4) Several MO calculations at different levels of theory have addressed the question of bonding in S_4N_4.[5]

(5) (a) Gleiter, R. *J. Chem. Soc. A* **1970**, 3174. (b) Gobinathan, M. S.; Whitehead, M. A. *Can. J. Chem.* **1975**, *53*, 1343. (c) Salaneck, W. R.; Lin, J. W.-P.; Paton, A.; Duke, C. B.; Ceasar, G. P. *Phys. Rev. B* **1967**, *13*, 4517. (d) Salahub, D. R.; Messmer, R. P. *J. Chem. Phys.* **1976**, *64*, 2039. (e) Tanaka, K.; Yambe, T.; Tachibana, A.; Kato, H.; Fukui, K. *J. Chem. Phys.* **1978**, *82*, 2121. (f) Millefiori, S.; Millefiori, A. *Inorg. Chim. Acta* **1980**, *45*, L19. (g) Chivers, T.; Fielding, L.; Laidlaw, W. G.; Trsic, M. *Inorg. Chem.* **1979**, *18*, 3379. (h) Findlay, R. H.; Palmer, M. H.; Downs, A. J.; Egdell, R. G.; Evans, R. *Inorg. Chem.* **1980**, *19*, 1307. (i) Millefiori, A.; Millefiori, S. *J. Chem. Res. (S)* **1980**, 244. (j) Suontamo, R. J.; Laitinen, R. S. *J. Mol. Struct. (THEOCHEM)* **1995**, *336*, 55.

(6) (a) Bärnighausen; von Volkmann, T.; Jander, J. *Acta Crystallogr.* **1961**, *14*, 1079; **1962**, *15*, 615. (b) Folkerts, H.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1994**, 620, 1011.

(7) For instance, the oxidation of Se_4N_4 with AsF_5 leads to the cations $Se_3N_2^{2+}$.and $(Se_3N_2^{\bullet+})_2$.[8] Se_4N_4 has also been utilized in the preparation metal complexes of Se_3N^- and $Se_2N_2^{2-}$ anions [9] as well as in the synthesis of metal complexes containing a NSeCl ligand.[10]

(8) (a) Awere, E. G.; Passmore, J.; White, P. S.; Klapötke, T. *J. Chem. Soc., Chem. Commun.* **1989**, 1415. (b) Awere, E. G.; Passmore, J.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1993**, 299.

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(11) (a) Mikulski, C. M.; Russo, P. J.; Saran, M. S.; MacDiarmid, A. G.; Garito, A. F.; Heeger, A. J. *J. Am. Chem. Soc.* **1975**, *97,* 6358. (b). Cohen, M. J.; Garito, A. F.; Heeger, A. J.; MacDiarmid, A. G.; Mikulski, C. M.; Saran, M. S.; Kleppinger, J. *J. Am. Chem. Soc.* **1976**, *98*, 3844.

(12) Labes, M.; Love, P. Nichols, L. F. *Chem. Rev.* **1979**, *79*, 1.

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

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In this paper we describe in detail convenient syntheses for S_4N_4 and 1,5-$Se_2S_2N_4$.[14] They rely on the reagents $[(Me_3Si)_2N]_2S$ and $[(Me_3Si)_2N]_2Se$, which are readily prepared[15] and can be used as a source of the NEN (E = S, Se) fragment. We have previously reported that the reaction of $[(Me_3Si)_2N]_2Se$ and $SeCl_4$ provides a route to Se_4N_4.[16] We now find that treatment of $[(Me_3Si)_2N]_2S$ with a mixture of SCl_2 and SO_2Cl_2 produces S_4N_4 in good yields. The analogous reactions involving $[(Me_3Si)_2N]_2S$ and $SeCl_4$ or $[(Me_3Si)_2N]_2Se$ with a mixture of SCl_2 and SO_2Cl_2 result in the formation of 1,5-$Se_2S_2N_4$. This new hybrid chalcogen nitride has been identified by X-ray crystallography, Raman spectroscopy, NMR spectroscopy (^{77}Se and ^{14}N), and mass spectroscopy.

Experimental Section

General. All reactions were carried under an argon atmosphere. $(Me_3Si)_2NH$ (Aldrich), *n*-butyllithium (2.5 M in hexanes, Aldrich), and selenium tetrachloride ($SeCl_4$, E. Merck GmbH) were used without further purification. Sulfur dichloride (SCl_2, Fluka Chemie AG) was distilled over PCl_3, and sulfuryl chloride (SO_2Cl_2) was distilled over P_4O_{10} under an argon atmosphere. Se_2Cl_2 was prepared as described by Fehér.[17] $[(Me_3Si)_2N]_2S$ and $[(Me_3Si)_2N]_2Se$ were prepared from $(Me_3Si)_2NH$ by utilizing the methods of Wolmershäuser et al.[15a] and Roesky et al.,[15b] respectively. Both compounds were purified by distillation. Dichloromethane (E. Merck GmbH) and carbon disulfide (E. Merck GmbH) were dried by distillation under a nitrogen atmosphere over P_4O_{10} before use.

Preparation of S_4N_4. ***Caution!*** *Samples of S_4N_4 may be explosive under the influence of heat or mechanical stress. The solid crystalline product should be handled with great care. The reaction should not be carried out in a large scale.*

$[(Me_3Si)_2N]_2S$ (0.352 g, 1.00 mmol) was dissolved in dichloromethane (10 mL), and a mixture of SCl_2 (0.103 g, 1.00 mmol), and SO_2Cl_2 (0.135 g, 1.00 mmol) in dichloromethane (10 mL) was added dropwise at −78 °C. The reaction mixture was stirred overnight and allowed to warm slowly to room temperature. After the brown solution was filtered and the solvent removed by evaporation, an orange-brown powder was obtained. The crude product was recrystallized from toluene to give pale orange crystals. The total yield of S_4N_4 was 75% (0.138 g, 0.75 mmol).[18] The ^{14}N NMR spectrum showed only one resonance at −256 ppm.[19] IR: 928 vs, 768 w, 727 m, 700 vs, 630 w, 553 vs, 548 vs, 529 w. Raman: 763 vw, 719 m, 559 s, 519 w, 347 m, 215 vs, 197 vs.[21]

Preparation of $Se_2S_2N_4$. *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.*

Reaction a. A solution of $[(Me_3Si)_2N]_2S$ (0.352 g, 1 mmol) in CS_2 (10 mL) was added to a suspension of $SeCl_4$ (0.221 g, 1 mmol) in CS_2 (20 mL) 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 precipitate was removed by filtration and washed three times with CH_2Cl_2. The yield was 0.105 g (76% based on $Se_2S_2N_4$).[23]

Reaction b. $Se_2S_2N_4$ was also prepared by treating 10 mL of a CH_2Cl_2 solution of $[(Me_3Si)_2N]_2Se$ (0.400 g, 1 mmol) with 10 mL of a CH_2Cl_2 solution containing 0.103 g (1 mmol) SCl_2 and 0.135 g (1 mmol) SO_2Cl_2 at −70 °C. The reaction mixture was stirred overnight and the dark red slightly soluble precipitate was filtered and washed three times with CH_2Cl_2. The yield was 0.10 g (72% based on $Se_2S_2N_4$).[23]

Single crystals of $Se_2S_2N_4$ were obtained by carrying out reaction **b** at room temperature. The solution was allowed to stand for 3 days during which orange, almost spherical, crystals were formed. These crystals were used for the mass spectroscopic, vibrational spectroscopic, ^{14}N and ^{77}Se NMR spectroscopic, and crystallographic identification of the product, as discussed below.

Spectroscopy. The ^{14}N and ^{77}Se NMR spectra were recorded on a Bruker DPX 400 spectrometer operating at 28.911 and 76.410 MHz, 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 ca. 100 000 transients, and those for selenium contained ca. 35 000 transients. D_2O was used as an external ^{2}H lock and CH_3NO_2 and a saturated solution of SeO_2 as external references. The ^{14}N chemical shifts are 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 Raman spectra were obtained from solid samples at ca. −100 °C by using a Bruker IFS-66 spectrometer equipped with a FRA-16 Raman unit and a Nd:YAG laser.

Fundamental vibrations were calculated for Se_4N_4 and 1,5-$Se_2S_2N_4$ by using a general valence force-field approach.[24] The *F* matrix of Se_4N_4 contained six diagonal force constants and nine off-diagonal interaction force constants. The analogous force field for 1,5-$Se_2S_2N_4$ contained 18 force constants. The molecular geometry for Se_4N_4 was taken from the crystal structure determination[25] and that for 1,5-$Se_2S_2N_4$ was estimated on the basis of the structural data taken from S_4N_4 and Se_4N_4.[3,6] The initial values of the force constants were estimated from those of S_4N_4 [22a] and SeS_3N_2.[26] They were refined by adjusting the observed frequencies to the calculated values until no further change was observed.

X-ray Crystallography. Crystal data and details of the structure determination are given in Table 1. Diffraction data were collected on a Siemens *R*3*m* diffractometer at 293 K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters were determined by the least-squares refinement of 25 automatically centered reflections. Two reference reflections were used to monitor the stability of the crystal. Their intensities were recorded periodically after each

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[14] For preliminary reports, see: (a) Chivers, T.; Laitinen, R. S.; Maaninen, A.; Pyykkönen, S.; Siivari, J. *Univ. Oulu Rep. Ser. Chem.* **1993**, *42*, P18. (b) Maaninen, A.; Laitinen, R. S.; Chivers, T. *Phosphorus Sulfur Silicon Relat. Elem.* **1997**, *124/125*, 457.

[15] (a) Wolmerhäuser, G.; Brulet, C. R.; Street, G. B. *Inorg. Chem.* **1978**, *17*, 3586. (b) Bjorgvinsson, M.; Roesky, H. W.; Pauer, F.; Stalke, D.; Sheldrick, G. M. *Inorg. Chem.* **1990**, *29*, 5140.

[16] Siivari, J.; Chivers, T.; Laitinen, R. S. *Inorg. Chem.* **1993**, *32*, 1519.

[17] Feher, F. In *Handbuch der präparativen Anorganischen Chemie*, 3rd ed.; Brauer, G., Ed.; Ferdinand Enke Verlag: Stuttgart, 1975; Vol. 1, p 415.

[18] The preparation of $[(Me_3Si)_2N]_2S$ from $(Me_3Si)_2NH$ and n-BuLi proceeds via the formation of $(Me_3Si)_2NLi$.[15a] S_4N_4 was also prepared directly by treating 0.668 g (4.00 mmol) of $(Me_3Si)_2NLi$ dissolved in 20 mL of CH_2Cl_2 with a mixture of 0.412 g (4.00 mmol) of SCl_2 and 0.270 g (2.00 mmol) of SO_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-red solution, evaporation of the solvent and recrystallization from toluene, 0.055 g [30% yield based on the initial amount of $(Me_3Si)_2NH$] of S_4N_4 was obtained as pale orange crystals.

[19] The ^{14}N chemical shift is virtually identical with that reported by Chivers et al.[20]

[20] Chivers, T.; Oakley, R. T.; Scherer, O. J.; Wolmershäuser, G. *Inorg. Chem.* **1981**, *20*, 914.

[21] Both the IR and Raman spectra are consistent with those reported earlier for S_4N_4.[22]

[22] (a) Steudel, R. *Z. Naturforsch.* **1981**, *36A*, 850. (b) Butler, I. S.; Sawai, T. *Can. J. Chem.* **1977**, *55*, 3838. (c) Gowik, P. K.; Klapötke, T. M. *Spectrochim. Acta* **1990**, *46A*, 1371.

[23] The ^{77}Se NMR spectra indicated that Se_8 (615 ppm) is formed as a side product in both reactions a and b. The spectral assignment (see Results and Discussion) led to a product distribution of 91% of $Se_2S_2N_4$ and 9% of Se_8 in both reactions. Anal. Calcd for this mixture: N, 16.45; S, 18.8; Se, 64.8. Found: N, 16.52 [reaction a] and 16.45 [reaction b].

[24] McIntosh, D. F.; Peterson, M. R. *General Vibrational Analysis Programs Utilizing the Wilson GF Matrix Method for a General Unsymmetrized Molecule*; QCPE Program No. 342; University of Indiana: Bloomington, IN, 1977.

[25] The bond parameters observed in the crystal structures[6] were averaged to preserve the ideal symmetry of D_{2d}.

[26] Maaninen, A.; Siivari, J.; Suontamo, R. J.; Konu, J.; Laitinen, R. S.; Chivers, T. *Inorg. Chem.* **1997**, *36*, 2170 and references therein.

Table 1. Crystal Data and Structure Refinement for 1,5-$Se_2S_2N_4$

molecular formula	$Se_2S_2N_4$
fw	278.08
cryst syst	monoclinic
a (Å)	8.818(2)
b (Å)	7.387(1)
c (Å)	8.981(2)
β (deg)	93.14(3)
V (Å^3)	584.1(2)
Z	4
space group	$P2_1/n$
T (K)	293(2)
λ(Mo Kα) (Å)	0.710 73 Å
ρ_{calc} (g/cm^3)	1.60
μ (mm^{-1})	13.259
F(000)	512
crystal size (mm)	0.20 × 0.20 × 0.15 mm
θ range for data collection (deg)	3.15−25.00
index ranges	$0 \le h \le 10$, $0 \le k \le 8$, $-10 \le l \le 10$
no. of reflcns collected	1100
no. of indep reflcns	1031 [R(int) = 0.0448]
no. of obsd reflcns [$I > 2\sigma(I)$]	649
refinement method	full-matrix least-squares on F^2
no. of data/restraints/parameters	1031/0/78
goodness-of-fit on F^2	0.924
R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0541$, w$R_2 = 0.1279^b$
R indices (all data)^a	$R_1 = 0.0994$, w$R_2 = 0.1424^b$
largest diff. peak and hole (e Å^{-3})	0.837 and −0.807

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [b] $w = [\sigma^2(F_o^2) + (0.0792P)^2]^{-1}$, where $P = \{\max(F_o^2,0) + 2F_c^2\}/3$.

batch of 98 data. The decay of the crystal appeared to be negligible during the data collection. The total number of 1031 independent reflections were collected in the 2θ range 6−50° of which 649 were considered observed [$I > 2\sigma(I)$]. Their net intensities were corrected for Lorentz and polarization effects.

Since the crystal was isostructural with S_4N_4 [3] and β-Se_4N_4,[6b] the initial atomic coordinates were taken from the crystal structure determination of S_4N_4.[3] The structure was refined using SHELXL-97.[27] It became apparent early in the refinement that the chalcogen atom positions were disordered with sulfur and selenium statistically distributed over the atomic sites. Therefore, the site occupation factors of sulfur and selenium were refined along the positional and thermal parameters. Because of the correlation between the thermal parameters and the occupation factors, the following constraints need to be applied:

$$sof_{Se(i)} + sof_{S(i)} = 1$$

$$U_{Se(i)} = U_{S(i)}$$

where $sof_{Se(i)}$, $sof_{S(i)}$, $U_{Se(i)}$, and $U_{S(i)}$ are the site occupation factors and the thermal parameters (isotropic or anisotropic) of selenium and sulfur at the ith atomic position. The estimation of the electron density, and thus the site occupation factors of sulfur and selenium at the given chalcogen atom position necessitates the constraining of the corresponding sulfur and selenium atoms in the same position. The scattering factors for the neutral atoms were those incorporated with the programs.

Fractional coordinates, isotropic thermal parameters, anisotropic thermal parameters, and all bond parameters are available as Supporting Information.

Results and Discussion

Preparation of S_4N_4. Tetrasulfur tetranitride can conveniently be prepared in good yields by the reaction of $[(Me_3Si)_2N]_2S$ with SCl_2 and SO_2Cl_2 in CH_2Cl_2:

$$[(Me_3Si)_2N]_2S + SCl_2 + SO_2Cl_2 \rightarrow \ ^1/_2S_4N_4 + 4\,Me_3SiCl + SO_2 \quad (1)$$

Purification by recrystallization from toluene yielded pale orange crystals that were identified as S_4N_4 by ^{14}N NMR, IR, and Raman spectroscopy. The ^{14}N NMR spectrum showed only one resonance at −256 ppm.[19] Both IR and Raman spectra of S_4N_4 are in good agreement with those reported earlier.[22]

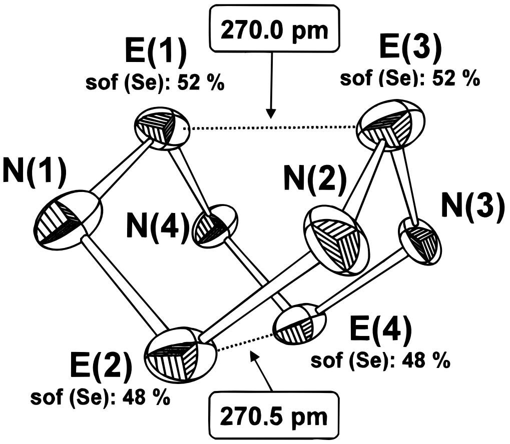

Figure 1. Molecular structure of 1,5-$Se_2S_2N_4$. Thermal ellipsoids are drawn at 50% probability level. The refined site occupation factors [$sof_{Se(i)}$] in disordered chalcogen atom positions [$E(i)$] are indicated in the figure ($sof_{S(i)} = 1 - sof_{Se(i)}$).

S_4N_4 has traditionally been prepared by the treatment of S_2Cl_2 with Cl_2 gas in CCl_4 followed by the reaction of the product with NH_3 gas.[28] An aqueous workup procedure is necessary to remove NH_4Cl.[29] The reduction of various N−S−Cl compounds also leads to S_4N_4.[31,32] The synthesis described in this work (see eq 1) provides an attractive route to good yields of S_4N_4, which utilizes easily prepared starting materials, avoids the use of gaseous reactants, and employs a simple purification procedure.

Preparation, Crystal Structure, and Spectroscopic Characterization of $Se_2S_2N_4$. The reaction of $[(Me_3Si)_2N]_2S$ with $SeCl_4$ in CH_2Cl_2 produces $Se_2S_2N_4$ as shown in eq 2.

$$[(Me_3Si)_2N]_2S + SeCl_4 \rightarrow \ ^1/_2Se_2S_2N_4 + 4\,Me_3SiCl \quad (2)$$

The same compound can also be obtained by the reaction of $[(Me_3Si)_2N]_2Se$ with SCl_2 and SO_2Cl_2 in CH_2Cl_2 (eq 3):

$$[(Me_3Si)_2N]_2Se + SCl_2 + SO_2Cl_2 \rightarrow \ ^1/_2Se_2S_2N_4 + 4\,Me_3SiCl + SO_2 \quad (3)$$

The product was obtained as dark brown-red powder, which was almost insoluble in organic solvents. Both reactions produce impure $Se_2S_2N_4$ in good yields (ca. 75%). The elemental analysis of the solid product from both reactions indicates a mixture containing $Se_2S_2N_4$ (91%) and Se (9%).[23]

The molecular structure of $Se_2S_2N_4$ with the atomic numbering scheme is shown in Figure 1. The molecule has a cage structure similar to those of S_4N_4[3] and Se_4N_4.[6] The refined site occupation factors of selenium in all chalcogen-atom positions are near 50%. Consequently, all bond lengths [1.75(1)−1.80(1) Å] show intermediate values between those of S_4N_4

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(27) Sheldrick, G. S. *SHELXL-97*; University of Göttingen: Germany, 1997.
(28) Villena-Blanco, M.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 98.
(29) A procedure has also been described by using CH_2Cl_2 as the solvent instead of CCl_4.[30]
(30) O'Hare, P. A. G.; Awere, E. G.; Parsons, S.; Passmore, J. *J. Chem. Thermodyn.* **1989**, *21*, 153.
(31) (a) Banister, A. J.; Fielder, A. J.; Hey, R. G.; Smith, N. R. M *J. Chem. Soc., Dalton Trans.* **1980**, 1457. (b) Berthet, M. P.; Vincent, H.; Monteil, Y. *Z. Naturforsch.* **1980**, *35B*, 329.
(32) For example, the treatment of $(NSCl)_3$ with iron turnings in monoglyme produces S_4N_4 in 67% yield.[31a]

Table 2. Calculated and Observed Fundamental Vibrations (cm^{-1}) of S_4N_4, 1,5-$Se_2S_2N_4$, and Se_4N_4

S_4N_4 (D_{2d})[a]				1,5-$Se_2S_2N_4$ (C_{2v})				Se_4N_4 (D_{2d})			
	Calc.	Obs.[b]	Assignment (%)[c]		Calc.	Obs	Assignment (%)[c]		Calc.	Obs.[b,d]	Assignment (%)[c]
a_1	717	720 m	48 ν_{SN}, 45 δ_{SNS}	a_1	636	624 vs	47 δ_{NSN}, 26 ν_{SeN}, 17 δ_{SNSe}	a_1	623	621 w	56 δ_{SeNSe}, 30 ν_{SeN}
a_1	552	558 s	51 ν_{SN}, 25 δ_{SNS}, 21 δ_{NSN}	a_1	523	517 vw	39 ν_{SeN}, 34 ν_{SN}, 14 δ_{NSeN}	a_1	318	318 w	40 ν_{SeN}, 34 ν_{SeSe}, 21 δ_{SeNSe}
a_1	229	218 s	54 δ_{NSN}, 33 ν_{SS}, 13 δ_{SNS}	a_1	255	269 m	30 ν_{SS}, 22 δ_{NSeN}, 13 ν_{SN}, 10 δ_{SNSe}, 10 τ	a_1	171	154 vs	48 δ_{NSeN}, 28 ν_{SeN}, 13 ν_{SeSe}, 10 δ_{SeNSe}
a_2	928	-	100 ν_{SN}	a_2	839	845 vw	83 ν_{SN}, 14 δ_{SNSe}	a_2	791	-	100 ν_{SeN}
a_2	254	-	100 τ	a_2	291	286 m	96 τ	a_2	170	-	100 τ
b_1	886	-	78 ν_{SN}, 22 δ_{SNS}	a_2	597	578 m	73 ν_{SeN}, 16 ν_{SN}	b_1	780	-	53 δ_{SeNSe}, 45 ν_{SeN}
b_1	227	224 m	86 δ_{SNS}, 13 ν_{SN}	a_2	162	160 vs	86 δ_{SNSe}	b_1	150	-	65 δ_{SeNSe}, 34 ν_{SeN}
b_2	762	765 m[e]	73 ν_{SN}, 25 δ_{NSN}	a_1	803	802 vw	61 ν_{SN}, 18 δ_{NSeN}, 14 δ_{SNSe}	b_2	538	534 m[e]	82 ν_{SeN}, 15 δ_{NSeN}
b_2	549	550 vs[d]	40 δ_{NSN}, 38 τ, 21 ν_{SN}	a_1	403	428 m	49 ν_{SeN}, 31 δ_{NSeN}, 12 δ_{SNSe}	b_2	426	425 m[e]	69 δ_{NSeN}, 20 τ, 10 ν_{SeN}
b_2	194	201 vs[e]	58 ν_{SS}, 23 τ, 17 δ_{NSN}	a_1	199	182 s	69 ν_{SeSe} 11 ν_{SS}, 20 τ	b_2	144	147 m[e]	56 ν_{SeN}, 41 ν_{SeSe}
e	925	925 vs[e]	82 ν_{SN}, 13 δ_{SNS}	b_2	862	856 vw	74 ν_{SN}, 14 δ_{SNSe}, 11 δ_{NSeN}	e	788	788 s[e]	57 ν_{SeN}, 33 δ_{SeNSe}
				b_1	727	726 w	84 ν_{SN}, 13 δ_{SNSe}				
e	708	701 vs[e]	82 ν_{SN}, 13 δ_{SNS}	b_1	675	692 w	39 ν_{SeN}, 32 δ_{NSN}, 16 δ_{SNSe}, 10 ν_{SN}	e	567	570 vs[e]	73 ν_{SeN}, 26 δ_{SeNSe}
				b_2	547	558 m	62 ν_{SeN}, 25 ν_{SN}, 10 δ_{SNSe}				
e	528	524 sh[e]	54 δ_{NSN}, 23 δ_{SNS}, 18 τ	b_1	479	490 m	48 ν_{SeN}, 41 δ_{NSN}, 10 ν_{SN}	e	306	310 m[e]	88 δ_{NSeN}
				b_2	420	405 w	65 δ_{NSeN}, 34 ν_{SeN}				
e	348	344 vs[e]	44 δ_{SNS}, 33 τ, 18 ν_{SN}	b_1	313	309 s	47 δ_{SNSe}, 31 τ, 11 δ_{SNS}	e	253	260 s[e]	49 ν_{SeN}, 29 τ, 16 δ_{SeNSe}
				b_2	234	221 w	57 δ_{SNSe}, 32 τ				

[a] The data are taken from ref 22a. [b] The observed vibrations are based on the Raman spectra except where otherwise indicated. [c] The assignment is based on the most significant contributions (>10%) in the potential energy distribution. [d] References 22c and 36. [e] IR data.[36]

and Se_4N_4 and reflect only the composition of the atomic positions (see Supporting Information). This is well exemplified by the transannular chalcogen−chalcogen contacts. In the present structure the two distances are 2.700(3) and 2.705(3) Å (see Figure 1) that fall between the S···S distances (2.597 and 2.601 Å) found in S_4N_4[3c] and the Se···Se distances (2.740−2.742 Å) found in α-Se_4N_4[6a] and *β*-Se_4N_4.[6b,33]

The observed disorder in the chalcogen atom sites indicates that either the lattice contains $Se_2S_2N_4$ molecules that can assume different orientations, or that the crystalline phase is in fact a solid solution containing 50% of both S_4N_4 and Se_4N_4. From the crystal structure determination alone it is not possible to distinguish between these two alternatives.

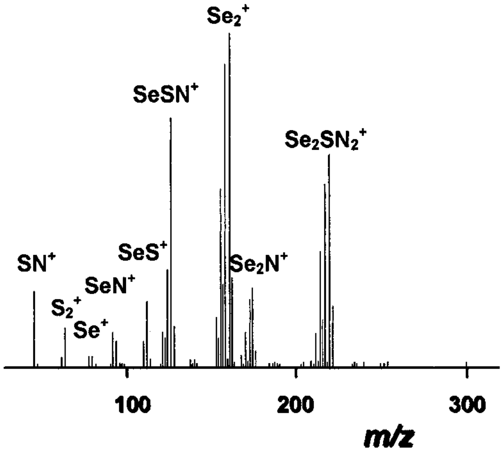

Figure 2. 12 eV EI mass spectrum of $Se_2S_2N_4$.

The 12 eV mass spectrum is shown in Figure 2. The fragment with the highest mass is $Se_2SN_2^+$. The observed and calculated isotopic distributions are in excellent agreement with each other (see Supporting Information). The fragmentation pattern implied by Figure 2 is also consistent with the molecular composition $Se_2S_2N_4$. The appearance of an $Se_2SN_2^+$ fragment in the mass spectrum rules out the possibility that the crystalline sample is a solid solution of S_4N_4 and Se_4N_4. Furthermore, the mass spectrum shows no evidence of the parent peaks for S_4N_4 and Se_4N_4.

The ^{14}N and ^{77}Se NMR spectra are recorded in CS_2. The ^{14}N NMR spectrum shows a single resonance at −238 ppm. This value is reasonable for $Se_2S_2N_4$ when compared to −256 ppm observed for S_4N_4.[19] The ^{77}Se NMR spectrum also exhibits a

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(33) The intensity data collections of S_4N_4[3c] and Se_4N_4[6] were carried out at −120 °C, while the present structure has been determined at room temperature. The internuclear distances are therefore not exactly comparable.

Table 3. Comparison of Selected Stretching Force Constants of 1,5-$Se_2S_2N_4$ with Some Related Species (N m^{-1})

force constant	1,5-$Se_2S_2N_4$	S_4N_4[a]	Se_4N_4	S_4N_2[b]	SeS_3N_2[b]	S_7NH[c]	$S_4(NH)_4$[d]	$S_3N_2^{2+}$[e]	$Se_2SN_2^{2+}$[e]	$Se_3N_2Cl^+$[f]
f_{S-N}	355	376		249	286	398	401	333[g]	339[g]	
f_{Se-N}	252		252							220,231
$f_{S=N}$				476	424			443[h]		
$f_{Se=N}$									425	391
$f_{S\cdots S}$	36	21								
$f_{Se\cdots Se}$	78		76							

[a] Reference 22a. [b] Reference 26. [c] Reference 37. [d] Reference 38. [e] Reference 39. [f] Reference 40. [g] The estimated bond order is 1.6−1.7. [h] The estimated bond order is 1.95.

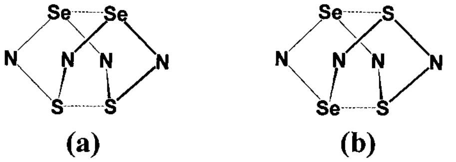

Figure 3. The (a) 1,5- and (b) 1,3-isomers of $Se_2S_2N_4$

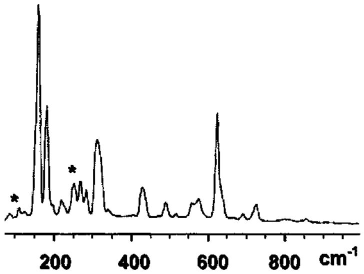

Figure 4. Raman spectrum of $Se_2S_2N_4$ recorded at ca. −100 °C. The signals marked with an asterisk are due to Se_8.[41]

single resonance at 1418 ppm. The ^{77}Se chemical shift of tetraselenium tetranitride has not been recorded owing to the insolubility of the binary material.

The appearance of only one resonance in the ^{14}N NMR spectrum indicates that all nitrogen atoms are equivalent implying the existence of 1,5-$Se_2S_2N_4$ rather than that of 1,3-$Se_2S_2N_4$ in the sample solution (see Figure 3).[34] In the case of the 1,3-isomer three resonances at the intensity ratio of 1:2:1 are expected in the ^{14}N NMR spectrum. Both isomers should exhibit only one ^{77}Se resonance. The two preparative methods also imply the formation of 1,5-$Se_2S_2N_4$. The formation of 1,3-$Se_2S_2N_4$ seems less likely, since it would require extensive rearrangement of the atoms and bonds during the reaction.[35]

Vibrational analysis provides further verification for the identity of the 1,5-isomer of $Se_2S_2N_4$. The Raman spectrum is shown in Figure 4. The molecule belongs to the point group C_{2v} and therefore all 18 fundamental vibrations ($6a_1$, $4a_2$, $4b_1$, $4b_2$) are both Raman and IR active. The assignment of the spectrum has been carried out by calculating the fundamental vibrations for 1,5-$Se_2S_2N_4$ using the general valence force field approach.[24] These calculations yield a good agreement with the observed Raman lines (see Table 2). The reliability of the assignment can be assessed by comparing it with the assignments for S_4N_4 and Se_4N_4.

Both tetrasulfur tetranitride and tetraselenium tetranitride belong to the point group D_{2d} and show twelve Raman active vibrations ($3a_1$, $2b_1$, $3b_2$, and 4e) and seven IR active vibrations ($3b_2$ and 4e). The two a_2 modes are inactive. Steudel[22a] has performed an extensive normal coordinate treatment for tetrasulfur tetranitride with a modified Urey−Bradley force field. To date, these calculations yield the most reliable assignment for both Raman and IR spectra of S_4N_4. Our present general valence force field calculations for Se_4N_4 produce an assignment with very similar potential energy distribution for all corresponding fundamental vibrations (see Table 2).

The assignment of the Raman spectrum of 1,5-$Se_2S_2N_4$ is consistent with those made for both S_4N_4 and Se_4N_4. When the symmetry is lowered from D_{2d} to C_{2v} the symmetry modes transform as follows: $a_1 \rightarrow a_1$, $a_2 \rightarrow a_2$, $b_1 \rightarrow a_2$, $b_2 \rightarrow a_1$, and $e \rightarrow b_1 + b_2$. This leads to the correlation between the fundamental vibrations of S_4N_4, 1,5-$Se_2S_2N_4$, and Se_4N_4 shown in Table 2. The potential energy distribution in each group of correlated vibrations is rather similar in all three molecules and indicates that the assignments of the vibrational spectra of the three species are consistent with each other. The force field calculations also yield reasonable force constants for 1,5-$Se_2S_2N_4$ and Se_4N_4. This is demonstrated in Table 3 by comparison of the stretching force constants of the present molecules with those of the related compounds.

Conclusions

The new chalcogen nitride $Se_2S_2N_4$ has been prepared in good yields by two methods. The crystal structure and spectroscopic (^{14}N and ^{77}Se NMR, mass, and Raman) data are consistent with the formation of the 1,5-isomer, which is a potential precursor, via thermolysis, of the four-membered ring $SeSN_2$ and, hence, the mixed chalcogen nitride polymer $(SeSN)_x$.

Acknowledgment. The financial support from the Academy of Finland is gratefully acknowledged.

Supporting Information Available: The observed and calculated isotopic distribution factors for $Se_2SN_2^+$ and an X-ray crystallographic file, in CIF format, are available free of charge via the Internet at http://pubs.acs.org.

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(34) In principle the ^{77}Se and ^{14}N chemical shifts could also be assigned to Se_4N_4, but that would necessitate the appearance of the ^{14}N resonance at −256 ppm due to S_4N_4 in the spectrum.

(35) The reaction 2 forms the cyclic eight-atom molecule from two NSN and two Se fragments and the reaction 3 from two NSeN and two S fragments. Therefore, in both cases 1,5-$Se_2S_2N_4$ should be formed rather than 1,3-$Se_2S_2N_4$.

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