Preparation, Crystal Structure, and Spectroscopic Characterization of $[(Se_2SN_2)Cl]_2$

Arto Maaninen,[†] Jari Konu,[†] Risto S. Laitinen,*,[†] Tristram Chivers,[‡] Gabriele Schatte,[‡] Jarkko Pietikäinen,[†] and Markku Ahlgrén[§]

Departments of Chemistry, 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 Joensuu,
P.O. Box 111, 80101 Joensuu, Finland

Received February 2, 2001

The reaction of $[(Me_3Si)_2N]_2S$ with an equimolar amount of $SeCl_4$ in dioxane at 50 °C affords $[(Se_2SN_2)Cl]_2$ (**1**) in excellent yield. Crystals of **1** are orthorhombic, space group *Pbca*, with $a = 8.5721(7)$ Å, $b = 7.8336(6)$ Å, $c = 15.228(1)$ Å, and $Z = 8$. The crystal structure contains two planar $Se_2SN_2^{\bullet+}$ rings which are linked by intermolecular Se···Se interactions [d(Se−Se) = 3.0690(7) Å]. The EI mass spectrum shows $Se_2SN_2^{\bullet+}$ as the fragment of highest mass. Both the ^{14}N and ^{77}Se NMR spectra show a single resonance (−52 and 1394 ppm, respectively). The solid $[(Se_2SN_2)Cl]_2$ gives a strong ESR signal indicating the presence of a $Se_2SN_2^{\bullet+}$ radical. The Raman spectrum was assigned through normal coordinate treatment involving a general valence force field. The vibrational analysis yielded a good agreement between the observed and calculated wavenumbers.

Introduction

Silicon−nitrogen compounds like $[(Me_3Si)_2N]_2S$[1] and $[(Me_3Si)_2N]_2Se$[2−4] are versatile reagents in chalcogen−nitrogen chemistry.[5−9] They can be converted to a variety of compounds upon treatment with chalcogen chlorides. For instance, the reaction of $[(Me_3Si)_2N]_2Se$ with selenium tetrachloride is a simple and convenient route to tetraselenium tetranitride, Se_4N_4,[10] and the treatment of $[(Me_3Si)_2N]_2S$ with a mixture of SCl_2 and SO_2Cl_2 produces tetrasulfur tetranitride, S_4N_4, in a good yield.[11] Analogous reactions involving $[(Me_3Si)_2N]_2S$ and $SeCl_4$ or $[(Me_3Si)_2N]_2Se$ and an equimolar mixture of SCl_2 and SO_2Cl_2 result in the formation of 1,5-$Se_2S_2N_4$.[11] Wolmershäuser et al.[12] have reported that the reaction of $[(Me_3Si)_2N]_2S$ with a 2:1 mixture of $SeCl_4$ and Se_2Cl_2 affords $[(Se_2SN_2)Cl]_2$ and identified the product by vibrational spectroscopy.

Zibarev et al.[13] have reported that the reaction between $[(Me_3Si)_2N]_2S$ and $SeCl_4$ in dioxane at 50 °C produces $Se_2S_2N_2Cl_2$ and proposed that it contains a six-membered ring. However, the characterization of this species was incomplete. We have published the preparation of 1,5-$Se_2S_2N_4$ using the same reagents and molar ratios.[11] We now describe a more detailed investigation of this reaction, which revealed that both 1,5-$Se_2S_2N_4$ and $[(Se_2SN_2)Cl]_2$ are formed. Their relative yields are dependent on the reaction conditions. The ionic compound $[(Se_2SN_2)Cl]_2$ was characterized by X-ray crystallography, Raman spectroscopy, ^{77}Se and ^{14}N NMR spectroscopy, mass spectroscopy, and ESR spectroscopy.

Experimental Section

General Procedures. All reactions and manipulations of air- and moisture-sensitive reagents were carried out under argon that had previously been passed through a bed of P_4O_{10}. $(Me_3Si)_2NH$ (Aldrich), *n*-butyllithium (2.5 M in hexanes, Aldrich), elemental selenium (Aldrich), and selenium tetrachloride $SeCl_4$ (E. Merck GmbH) were used without further purification. $[(Me_3Si)_2N]_2S$ was prepared from $(Me_3Si)_2NH$ by using the synthetic method of Wolmershäuser et al.[12] The compound was purified by distillation. Dioxane and carbon disulfide (E. Merck, GmbH) were dried by distillation over sodium and P_4O_{10}, respectively, under an argon atmosphere prior to use.

Spectroscopic Methods. 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 14.49 and 90.09 kHz, yielding the spectral resolutions of 14.2 and 2.75 Hz/data point, respectively. The pulse widths were 12.0 and 6.70 μs for ^{14}N and ^{77}Se, respectively, corresponding to bulk magnetization tip angles of 44° and 46°, respectively. The ^{77}Se pulse delay was 2.0 s. A total of 10000−100000 ^{14}N transients and 10000−35000 ^{77}Se transients were accumulated. The spectra were recorded unlocked. The ^{14}N NMR chemical shifts are reported relative to CH_3NO_2. All ^{77}Se NMR spectra were referenced externally to a saturated solution of SeO_2 in D_2O. The chemical shifts are reported relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$].[14]

MS-EI mass spectra were recorded by using a Micromass Quattro II spectrometer at 70 eV of electron energy. The Raman spectra were obtained from solid samples at room temperature by using a Bruker IFS-66 spectrometer equipped with a FRA-16 Raman unit and a Nd:

[†] University of Oulu.

[‡] University of Calgary.

[§] University of Joensuu.

(1) Wannagat, U.; Kucketz, H. *Angew. Chem.* **1962**, *74*, 117.

(2) Haas, A.; Kasprowski, J. *Chimia* **1990**, *44*, 57.

(3) Haas, A.; Kasprowski, J.; Angermund, K.; Betz, P.; Kruger, C.; Tsay, Y.-H.; Werner, S. *Chem. Ber.* **1991**, *124*, 1895.

(4) Björgvinsson, M.; Roesky, H. W.; Pauer, F.; Stalke, D.; Sheldrick, G. M. *Inorg. Chem.* **1990**, *29*, 5140.

(5) Chivers, T. In *The Chemistry of Inorganic Homo- and Heterocycles*; Academic Press Inc.: London, 1987; Vol. 2, pp 793−869.

(6) (a) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, *36*, 299. (b) Klapötke, T. In *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Elsevier Science Publishers B.V.: Amsterdam, 1992; Chapter 20.

(7) Björgvinsson, M.; Roesky, H. W. *Polyhedron* **1992**, *10*, 2353.

(8) Haas, A.; Kasprowski, J.; Pryka, M. *Coord. Chem. Rev.* **1994**, *130*, 301.

(9) Chivers, T. *Main Group. Chem. News* **1993**, *1*, 6.

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

(11) Maaninen, A.; Laitinen, R. S.; Chivers, T.; Pakkanen, T. A. *Inorg. Chem.* **1999**, *38*, 3450.

(12) Wolmershäuser, G.; Brulet, C. R.; Street, G. B. *Inorg. Chem.* **1978**, *17*, 3586.

(13) Zibarev, A. V.; Furin, G. G.; Yakobson G. G. *Izv. Akad. Nauk Ser. Khim.* **1985**, *12*, 2774.

(14) Burns, R. C.; Collins, M. J.; Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1986**, *25*, 4465.

10.1021/ic010141h CCC: \$20.00

YAG laser (power 130 mW; 32 scans; spectral resolution ±2 cm^{-1}; Blackmann−Harris four-term apodization, no white light correction).

Fundamental vibrations were calculated for the $Se_2SN_2^{\bullet+}$ ring[15] by using a general valence force-field approach.[16] The *F* matrix contained seven diagonal force constants. The molecular geometry of $Se_2SN_2^{\bullet+}$ was symmetrized to the point group C_{2v} based on the bond parameters from the crystal structure determination. The initial values of the force constants were estimated from those of the related molecules.[17−20] They were refined by adjusting the calculated frequencies to the observed values until no further change was observed.

The ESR spectrum of solid $[(Se_2SN_2)Cl]_2$ was recorded in a 4 mm quartz tube sealed under argon at room temperature on a Bruker 300e spectrometer equipped with a NMR magnetometer, a microwave counter, and a variable-temperature accessory. Spectral simulations were carried out using the WINEPR SimFonia program provided by Bruker.

Preparation of $[(Se_2SN_2)Cl]_2$. *CAUTION! Dry 1,5-$Se_2S_2N_4$ is explosive under the influence of heat or mechanical stress. It is also possible that $[(Se_2SN_2)Cl]_2$ decomposes violently. The products should therefore be stored and handled under hydrocarbon solvents and their preparation limited to amounts <0.1 g.*

$[(Me_3Si)_2N]_2S$ (0.704 g, 2.00 mmol) was dissolved in dioxane (10 mL) and added dropwise to a suspension of $SeCl_4$ (0.442 g, 2.00 mmol) in dioxane (20 mL) at 50 °C. The reaction mixture was stirred for 8 h at 50 °C and allowed to cool slowly to room temperature to give very dark red (almost black) crystals that are slightly soluble in common organic solvents. The yield was 0.244 g (94% based on the initial amount of selenium[21]). MS (%, *m/z*):[22] 220 (21, $Se_2SN_2^+$), 174 (15, Se_2N^+), 160 (13, Se_2^+), 126 (53, $SeSN^+$), 94 (39, SeN^+), 80 (63, Se^+), 46 (100, SN^+). The crystals of $[(Se_2SN_2)Cl]_2$ could be hand-picked under a microscope and were used for the determination of vibrational, ^{14}N and ^{77}Se NMR, and ESR spectra and for the crystallographic characterization of the product.

Preparation of Monoclinic α-Se_8. Red crystals of Se_8 for the low-temperature crystal structure determination were obtained by the recrystallization of vitreous selenium from CS_2.

X-ray Crystallography. Crystal data and details of the structure determination for $[(Se_2SN_2)Cl]_2$ (**1**) and monoclinic α-Se_8 (**2**) are given in Table 1. Diffraction data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by recording 360 frames via φ-rotation ($\Delta\varphi = 1°$; two times 40 s per frame). The total of 1003 unique reflections ($3.58° < \theta < 25.99°$) were recorded for **1** of which 891 had $I > 2.00\sigma(I)$. In the case of **2** there were 1649 ($2.89° < \theta < 25.35°$) and 2018 ($2.89° < \theta < 25.35°$) unique reflections for the data collection at −100 and −150 °C, respectively, of which 1084 and 1821 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 in the case of both compounds. The structure was solved by direct methods using SHELXS-97[23] and refined using SHELXL-97.[24] The scattering factors for the neutral atoms were those incorporated with the programs.

Table 1. Crystal Data for $[(Se_2SN_2)Cl]_2\cdot$(**1**) and Monoclinic α-Se_8[a]

empirical formula	N_2SClSe_2	Se_8	
fw (g mol^{-1})	253.45	631.68	
cryst syst	orthorhombic	monoclinic	
T (°C)	−150(2)	−100(2)	−150(2)
a (Å)	8.5721(7)	8.894(2)	8.9247(2)
b (Å)	7.8336(6)	9.000(2)	8.9665(2)
c (Å)	15.228(1)	11.383(2)	11.3687(2)
β (deg)		90.68(2)	90.583(1)
V (Å^3)	1022.6(1)	911.1(3)	909.71(3)
Z	8	4	
space group	*Pbca*	$P2_1/n$	
ρ_{calc} (g/cm^3)	3.293	4.605	4.612
μ (mm^{-1})	15.23	32.00	32.05
F(000)	920	1088	
cryst size (mm^3)	0.25 × 0.20 × 0.03	0.25 × 0.15 × 0.15	0.25 × 0.15 × 0.05
R1[b] [$I > 2\sigma(I)$]	0.0287	0.0593	0.0445
wR2[c] (all data)	0.0547	0.1676	0.1153

[a] λ(Mo Kα) = 0.71073 Å. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

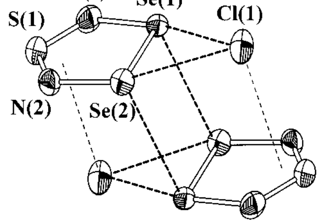


Figure 1. The molecular structure of $[(Se_2SN_2)Cl]_2$. Thermal ellipsoids are drawn at the 50% probability level.

Results and Discussion

Synthesis of $[(Se_2SN_2)Cl]_2$. The product distribution in the reaction of $[(Me_3Si)_2N]_2S$ and $SeCl_4$ is dependent on the reaction conditions. We have previously reported that it produces 1,5-$Se_2S_2N_4$ in carbon disulfide at −70 °C.[11] If the reaction is carried out at ambient temperature in either CS_2 or dichloromethane, it affords ca. 25% $[(Se_2SN_2)Cl]_2$ and 75% 1,5-$Se_2S_2N_4$. In dioxane at 50 °C, however, the product distribution is reversed: the reaction yields a mixture containing ca. 70% $[(Se_2SN_2)Cl]_2$ and 30% 1,5-$Se_2S_2N_4$ according to the ^{77}Se NMR spectrum of the reaction mixture. The formation of either 1,5-$Se_2S_2N_4$ or $[(Se_2SN_2)Cl]_2$, depending on the reaction conditions and on the molar ratio of the reagents, is consistent with the proposal of Haas et al.[3] that 1,5-$Se_2S_2N_4$ is an intermediate in the formation of the Se_2SN_2 ring upon treatment of $Se(NSO)_2$ with Lewis acids.

Crystal Structure. The structure of $[(Se_2SN_2)Cl]_2$ (**1**) with the atomic numbering scheme is shown in Figure 1. The cation of **1** consists of two planar symmetry-related five-membered rings $(Se_2SN_2)^{\bullet+}$ with two Se···Se close contacts connecting them to form a dimer, as in the case of $[(S_3N_2)Cl]_2$,[25] with which **1** is isostructural. The cations in $(Se_xS_{3-x}N_2)_2(AsF_6)_2$ ($x = 0-3$)[19,26−29] show similar dimeric arrangements of the five-membered rings.

Bond lengths and bond angles of **1** are summarized in Table 2. The S−N bond lengths in the NSN fragment [1.555(5) and

---

(15) The Se···Se interactions in the 10-atomic $(Se_2N_2S)_2^{2+}$ cation (see Figure 1) are sufficiently weak to enable the assignment of the Raman spectrum of the compound to be based on the force-field calculations of the fundamental vibrations of the five-membered Se_2N_2S ring. Similarly, the Se···Cl interactions can be ignored.

(16) 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, Bloomington, IN, 1977.

(17) Siivari, J.; Chivers, T.; Laitinen, R. S. *Inorg. Chem.* **1993**, *32*, 4391.

(18) Awere, E. G.; Passmore, J.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1993**, 299.

(19) Awere, E. G.; Brooks, W. V. F. Passmore, J.; White, P. S.; Sun, X.; Cameron, T. S. *J. Chem. Soc., Dalton Trans.* **1993**, 2439.

(20) Brooks, W. V. F.; Cameron, T. S.; Parsons, S.; Passmore, J.; Schriver, M. J. *Inorg. Chem.* **1994**, *33*, 6230.

(21) According to ^{77}Se NMR spectroscopy the crystalline material is a mixture containing 70% of $(Se_2N_2SCl)_2$ and 30% of 1,5-$Se_2S_2N_4$.

(22) The relative intensity refers to the peak of the highest intensity in the isotopic distribution pattern of a given fragment.

(23) Sheldrick, G. M. *SHELXS-97. Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

(24) Sheldrick, G. M. *SHELXL-97. Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(25) Small, R. W. H.; Banister, A. J.; Hauptman, Z. V. *J. Chem. Soc., Dalton Trans.* **1984**, 1377.

(26) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 3784.

(27) Banister, A. J.; Clarke, H. G.; Rayment, I.; Shearer, M. M. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 647.

(28) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 4053.

(29) Awere, E. G.; Passmore, J.; White, P. S.; Klapötke, T. *J. Chem. Soc., Chem. Commun.* **1989**, 1415.

Table 2. Selected Bond Lengths and Bond Angles for $[(Se_2SN_2)Cl]_2$ (**1**)

Bond Lengths (Å)			
S(1)−N(1)	1.556(4)	Se(1)−Se(2)	2.3464(7)
S(1)−N(2)	1.557(4)	Se(1)···Cl(1)	2.907(4)
N(1)−Se(1)	1.792(4)	Se(2)···Cl(1)	2.916(4)
N(2)−Se(2)	1.807(4)	Se(1)···Se(2)[a]	3.0690(7)
Bond Angles (deg)			
N(1)−S(1)−N(2)	113.8(2)	N(1)−Se(1)−Cl(1)	159.4 (2)
S(1)−N(1)−Se(1)	119.4(2)	N(2)−Se(2)−Cl(1)	159.5 (2)
S(1)−N(2)−Se(2)	118.3(2)	N(2)−Se(2)−Se(1)[a]	110.0(1)
N(1)−Se(1)−Se(2)	93.9(1)	N(1)−Se(1)−Se(2)[a]	110.2(1)
N(2)−Se(2)−Se(1)	94.4 (1)		

[a] Symmetry operation: 1 − *x*, −*y*, 1 − *z*.

Table 3. Bond Lengths (Å) in Monoclinic α-Se_8 at −150, −100, and 26 °C

bonds	−150 °C	−100 °C	26 °C[a,b]
Se(1)−Se(2)	2.327(1)	2.325(6)	2.346(5)
Se(2)−Se(3)	2.307(1)	2.295(6)	2.337(5)
Se(3)−Se(4)	2.310(1)	2.329(7)	2.333(5)
Se(4)−Se(5)	2.320(1)	2.306(6)	2.331(5)
Se(5)−Se(6)	2.293(1)	2.301(6)	2.332(4)
Se(6)−Se(7)	2.291(1)	2.339(6)	2.345(5)
Se(7)−Se(8)	2.269(1)	2.292(6)	2.326(4)
Se(8)−Se(1)	2.293(1)	2.303(6)	2.337(4)
av	2.301(18)	2.311(17)	2.336(7)

[a] Reference 35. [b] The numbering of the atoms has been modified to correspond to those determined in this work.

Table 4. Average Bond Lengths (Å) and Bond Orders[a] in $(E_3N_2)^{2+}$ and $(E_3N_2)^{\bullet+}$

	$(S_3N_2)^{n+}$ [a]	$(SeS_2N_2)^{n+}$ [b]	$(Se_2SN_2)^{n+}$		$(Se_3N_2)^{n+}$
6π-Electron Ring Cations (*n* = 2)					
S−S	2.09 *0.85*				
Se−S		2.25 *0.88*			
Se−Se			2.31 *1.10*		2.33 *1.03*
N═S═N	1.59 *1.68*	1.58 *1.73*	1.59 *1.68*		
N═Se═N					1.70 *1.91*
N−S	1.53 *2.04*	1.47 *2.48*			
N−Se		1.74 *1.68*	1.70 *1.91*		1.74 *1.68*
ref	20	19	44		18
7π-Electron Ring Cations (*n* = 1)					
S−S	2.13 *0.74*				
Se−S		2.27 *0.82*			
Se−Se			2.35[c] *0.91*	2.35[d] *0.85*	2.40 *0.82*
N═S═N	1.56 *1.85*	1.57 *1.79*	1.56[c] *1.85*	1.56[d] *1.85*	
N═Se═N					1.71 *1.85*
N−S	1.63 *1.48*	1.68 *1.25*			
N−Se		1.73 *1.73*	1.76[c] *1.42*	1.80[d] *1.25*	1.76 *1.57*
S···S	2.92 *0.06*				
Se···S		3.11 *0.05*			
Se···Se			3.14[c] *0.07*	3.07[d] *0.08*	3.14 *0.07*
ref	25	19	28	this work	29

[a] The bond order that is given in italics has been calculated by the Pauling equation $N = 10^{(D - R)/0.71}$,[42] where *R* is the observed bond length (Å). At room temperature the single-bond length *D* is estimated by the sums of appropriate covalent radii (Å):[43] Se−Se 2.34, Se−S 2.21, S−S 2.04 Å. At low temperatures the estimates of 1.716 Å[32] and 1.869 Å[4] have been utilized for the S−N and Se−N single-bond lengths, respectively. The average Se−Se bond length in Se_8 varies linearly in the temperature range −150 to +26 °C. Therefore, the estimate for the single-bond length at −150 °C is 2.30 Å from the crystal structure determination at that temperature, and that at −30 °C is 2.32 Å that is obtained through interpolation from the results of the crystal structure determinations at three different temperatures −150, −100, and 26 °C. [b] The bond distances and orders have been estimated by resolving the observed disorder in the crystals. [c] The data for $(Se_2SN_2)_2(AsF_6)_2$ are recorded at −30 °C.[27,28] [d] The data for $[(Se_2SN)Cl]_2$ (**1**) have been recorded at −150 °C.

1.557(7) Å] are similar to those in $(Se_2SN_2)_2(AsF_6)_2$ [1.54(1)−1.58(1) Å][28] and indicate double-bond character.[30] The corresponding bonds in $[(S_3N_2)Cl]_2$ [1.557(5) and 1.563(5) Å][25] and $(SeS_2N_2)_2(AsF_6)_2$ [1.55(1)−1.58(1) Å][19] are also in close agreement. The Se−N bonds [1.798(5) and 1.811(5) Å] are somewhat shorter than the Se−N single bond of 1.869(2) Å in $[(Me_3Si)_2N]_2Se$,[4] but slightly longer than the Se−N bond lengths of 1.75(1)−1.76(1) Å and 1.76(2) Å observed in $(Se_2SN_2)_2(AsF_6)_2$[28] and $(Se_3N_2)_2(AsF_6)_2$,[29] respectively. The corresponding S−N bonds in $[(S_3N_2)Cl]_2$ [1.618(4) and 1.642(4) Å][25] are also somewhat shorter than the single bonds. The Se−Se bond length of 2.3466(7) Å in **1** is in agreement with those in $(Se_2SN_2)_2(AsF_6)_2$ [2.345(2)−2.358(2) Å][28] and is close to the single-bond length. In contrast, the lengthening of the Se−Se bond [2.398(3)−2.395(3) Å] and the S−S bond [2.131(2) Å] in $(Se_3N_2)_2(AsF_6)_2$[29] and $[(S_3N_2)Cl]_2$,[25] respectively, with respect to the conventional single bonds seems to be somewhat more pronounced.[33] It should be noted, however, that while the X-ray data of $[(S_3N_2)Cl]_2$,[25] $(SeS_3N_2)_2(AsF_6)_2$,[19] and $(Se_3N_2)_2(AsF_6)_2$[29] have been recorded at room temperature, those of **1** have been recorded at −150 °C and those of $(Se_2SN_2)_2(AsF_6)_2$[28] at −30 °C. We have therefore redetermined the crystal structure of monoclinic α-Se_8 (**2**) at −100 and −150 °C in order to facilitate a better comparison of the Se−Se bond length in $[(Se_2SN_2)Cl]_2$ (**1**) and $(Se_2SN_2)_2(AsF_6)_2$ with the Se−Se single-bond length.

The structure of monoclinic α-Se_8 at all three temperatures is composed of discrete cyclic crown-shaped Se_8 molecules with structural features, as described by Cherin and Unger.[35] The Se−Se bond lengths at different temperatures are shown in Table 3. It can be seen that the individual bond lengths in the two low-temperature structures are significantly shorter than the corresponding bonds in the room temperature structure.[35] However, it is also evident in the bond lengths shown in Table 3 that the Se_8 ring becomes more distorted from the ideal D_{4d} symmetry as the temperature is lowered. Consequently, the bond length range and the standard deviations of the mean bond lengths are larger at −150 and −100 °C than at room temperature. The average Se−Se bond length of monoclinic α-Se_8 is 2.301(18), 2.311(17), and 2.336(7) Å[35] at −150, −100, and 26 °C, respectively. The average bond length varies linearly with temperature at this temperature range.

When all evidence in Table 3 is taken into account, it can be concluded that despite the large standard deviations in the average bond lengths at low temperature the Se−Se bonds in $[(Se_2SN_2)Cl]_2$ (**1**) and $(Se_2SN_2)_2(AsF_6)_2$[28] are lengthened with respect to the single bond in a fashion similar to other members of $(Se_xS_{3-x}N_2{}^{\bullet+})$ radical cations[19,25,29] (see Table 4).

The planar five-membered $(Se_xS_{3-x}N_2{}^{\bullet+})$ rings form a seven-π-electron system. Their bond lengths and bond orders have been compared in Table 4 with those of cyclic $(Se_xS_{3-x}N_2)^{2+}$

---

[30] The S═N double-bond length of 1.536(3) Å is exhibited by $Me_3Si-N{=}S{=}NSiMe_3$[31] and the single-bond length of 1.716(3) Å by $(Me_3Si)_2N-S-N(SiMe_3)_2$.[32]

[31] Anderson, D. G.; Robertson, H. E.; Rankin, D. W. H.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 859.

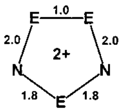
[32] Schubert, G.; Kiel, G.; Gattow, G. *Z. Anorg. Allg. Chem.* **1989**, *575*, 129.

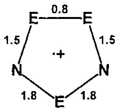
[33] The S−S single bond at room temperature is exemplified by 2.041(1)−2.049(1) Å observed in orthorhombic α-S_8,[34] and the Se−Se single bond of 2.326(4)−2.346(5) Å is represented in Se_8.[35] The bond parameters in other polymorphs of S_8[36−39] and Se_8[40, 41] are in close agreement.

[34] Coppens, P.; Yang, Y. W.; Blessing, R. H.; Cooper, W. F.; Larsen, F. K. *J. Am. Chem. Soc.* **1977**, *99*, 760.

[35] Cherin, P.; Unger, P. *Acta Crystallogr., Sect. B* **1972**, *28*, 313.

cations that are six-π-electron aromatic rings. The bond orders seem to be rather independent of the identity of the chalcogen atoms in the ring, but there is expectedly a trend depending on the charge of the species. The average bond orders across the two series are as follows (E = S, Se):





While the bond orders in the NEN fragments are approximately equal in both series of species, the bond orders of the E−E and E−N bonds in the NEEN fragments are higher, and consequently, the bonds are shorter in the dication than in the dimeric radical cation, as shown in Table 4. The bonding trends have been discussed in terms of the electronic structures of $(S_3N_2)^{2+}$ and $(S_3N_2)^{\bullet+}$.[18,20] The LUMO of $(S_3N_2)^{2+}$ is antibonding with respect to the S−N and S−S bonds in the NSSN fragment, but nonbonding with respect to the N=S bonds in the NSN fragment. The addition of one electron to this MO therefore weakens the two former bonds but has no effect on the N=S bonds. This explains the structural trends in $(Se_xS_{3-x}N_2)^{2+}$ and $(Se_xS_{3-x}N_2)^{\bullet+}$, assuming that their electronic structures are similar to those of $S_3N_2^{2+}$ and $S_3N_2^{\bullet+}$.[44]

While the qualitative inspection of the frontier orbitals accounts for the trends of the bond lengths in the two series of cations, it has been noted that the E−E bonds are surprisingly long in $(Se_xS_{3-x}N_2)^{2+}$ and $(Se_xS_{3-x}N_2)^{\bullet+}$.[18,20,44] The unexpectedly low bond orders have been attributed to the electrostatic repulsion between two adjacent, positively charged chalcogen atoms. Since the repulsion is expected to be larger across the S−S bond,[20] it accounts for the slightly lower bond orders in $(S_3N_2)^{\bullet+}$ and $(SeS_2N_2)^{\bullet+}$ than in selenium-rich cations, as shown in Table 4.

Two Se···Se close contacts of 3.0690(7) Å connect the two planar symmetry-related five-membered rings $(Se_2SN_2)^{\bullet+}$ of **1** into a dimer. The corresponding S···S close contact in $[(S_3N_2)Cl]_2$ is 2.916(2) Å.[25] The dihedral angle between the plane containing the Se_2N_2S ring and the plane with the cyclic Se_4 fragment is 110.2° (cf. 110.4° in $[(S_3N_2)Cl]_2$[25]). The chalcogen−chalcogen close contacts between the five-atomic rings in the various members of the series $(Se_xS_{3-x}N_2)_2(AsF_6)_2$ ($x = 0-3$) span a narrow range of 2.994−3.159 Å,[17,19,26,28,29] the shorter values being associated with S···S contacts. According to Awere et al.[18,29] the dimerization of the two $(E_3N_2)^{\bullet+}$ (E = S, Se) radical ions can be explained by the overlap of the chalcogen-based singly occupied π^* molecular orbitals.

The chloride anion Cl(1) and its symmetry-equivalent counterpart both lie in the same plane as one of the two five-membered rings of the cation of **1** (see Figure 1). The two Se···Cl contacts of 2.907(4) and 2.916(4) Å are expectedly shorter than the sum of van der Waals radii of 3.8 Å for selenium and chlorine.[43] It can also be seen from Figure 1 that Cl(1) lies directly above the N=S=N fragment of the second five-membered ring of the cation that is generated from the first ring by symmetry. The contact is characterized by a short distance of 3.298(5) Å between Cl(1) and S(1)[a] (see Table 2 for the definition of the symmetry operation *a*). This distance is comparable with that in $[(S_3N_2)Cl]_2$ [3.152(2) Å[25]].

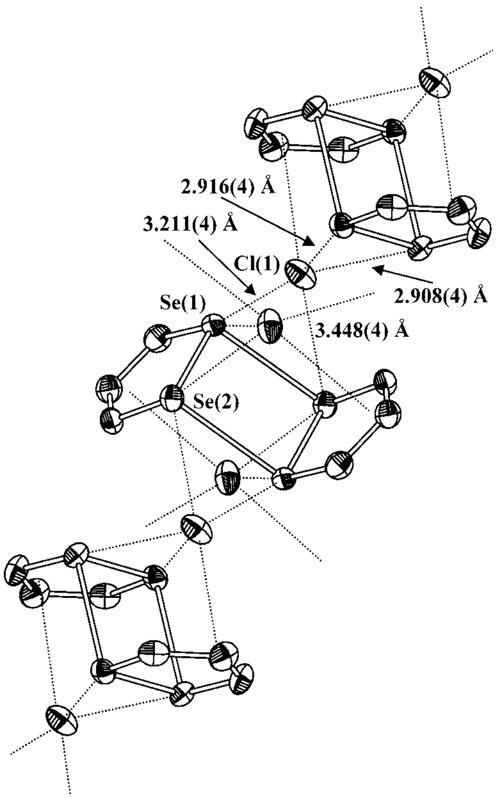


Figure 2. Interionic close contacts connect the $[(Se_2SN_2)Cl]_2$ units into a continuous three-dimensional network.

The chloride anion also exhibits two close contacts of 3.211(4) and 3.448(4) Å to the selenium atoms of the neighboring $(Se_2SN_2)_2^{2+}$ cation, resulting in approximate trigonal bipyramidal coordination around Cl(1), as shown in Figure 2. These close contacts link the $[(Se_2SN_2)Cl]_2$ units to form a continuous three-dimensional network. The packing in the isostructural $[(S_3N_2)Cl]_2$ is similar, with corresponding Cl···S contacts of 3.184(2) and 3.207(2) Å.[25] As discussed by Small et al.,[25] there must be a significant covalent contribution to the bonding involving chlorine in addition to electrostatic factors. The strong intermolecular interactions account for the low solubility of these species in organic solvents.

Spectroscopy. The EI mass spectrum of the crystalline product showed $Se_2N_2S^+$ (*m/z* 220) as the fragment with highest mass.[45] The fragmentation pattern is also consistent with that proposed by Wolmerhäuser et al.[12] and indicates the correct composition for **1**. The observed and calculated isotopic distributions in all fragments are in excellent agreement.

The ^{14}N and ^{77}Se NMR spectra of **1** were recorded in dioxane. The ^{14}N NMR spectrum shows a single resonance at −52 ppm. This value is reasonable for $(Se_2SN_2)^{\bullet+}$ containing a N=S=N

---

(36) Rettig, S. J.; Trotter, J. *Acta Crystallogr., Sect.* C **1987**, *43*, 2260.
(37) Templeton, L. K.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1976**, *15*, 1999.
(38) Goldsmith, L. M.; Strouse, C. M. *J. Am. Chem. Soc.* **1977**, *99*, 7580.
(39) Watanabe, Y. *Acta Crystallogr., Sect. B* **1974**, *30*, 1396.
(40) Marsh, R. E.; Pauling, L.; McCullough, J. D. *Acta Crystallogr.* **1953**, *6*, 71.
(41) Foss, O.; Janickis, V. J. *J. Chem. Soc., Dalton Trans.* **1980**, 624.
(42) Pauling, L. *The Nature of the Chemical Bond;* 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(43) Emsley, J. *The Elements*, 3rd ed.; Clarendon Press: Oxford 1998.
(44) Awere, E. G.; Passmore, J.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1992**, 1267; Erratum, **1992**, 2427.

(45) We have reported earlier that the 12 eV mass spectrum of crystalline 1,5-$Se_2S_2N_4$ recorded with an older KRATOS MS80 spectrometer also showed only $Se_2SN_2^+$ as the fragment with highest mass with no evidence of the molecular ion.[11] When the mass spectrum was redetermined with the Micromass Quattro II spectrometer, the molecular ion of $Se_2S_2N_4^+$ could be observed. The observed and calculated isotopic distributions were in accord with the chemical composition.

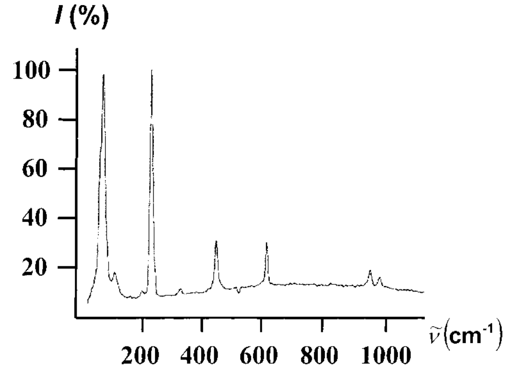


Figure 3. Raman spectrum of $[(Se_2SN_2)Cl]_2$ recorded at 23 °C.

Table 5. Calculated and Observed Fundamental Vibrations (cm^{-1}) of $Se_2SN_2^{+\bullet}$ and the Main Contributions in the Calculated Potential Energy Distribution (%) along the Internal Coordinates

obsd[a]	calcd	potential energy distribution[b]
980 (*4*)	978 b_2	91% ν_{SN}
951 (*7*)	954 a_1	69% ν_{SN}, 15% δ_{NSN}
627 (*18*)	626 a_1	54% δ_{NSN}, 28% ν_{SN}
470 (*22*)	473 b_2	90% ν_{SeN}
359 (*3*)	342 a_1	69% ν_{SeN}, 28% δ_{NSN}
269 (*100*)	268 a_1	97% ν_{SeSe}
240 (*3*)	241 b_1	74% τ_{SN}, 25% τ_{SeN}
155 (*9*)	148 a_2	58% τ_{SeN}, 26% τ_{SN}, 26 τ_{SeSe}
119 (*100*)	114 b_2	88% δ_{NSeSe}, 11% δ_{SeNS}

[a] The relative intensities of the Raman lines are given in italics in parentheses.[b]The contributions > 10% are included in the Table.

fragment.[46] It is also consistent with the ^{14}N chemical shifts of −68.9, −72.5, and −67.6 ppm recorded in $SO_2(l)$ for $(SeS_2N_2)^{2+}$,[19] $(Se_2SN_2)^{2+}$,[44] and $(Se_3N_2)^{2+}$,[18] respectively. The ^{77}Se NMR spectrum shows two resonances at 1394 and 1407 ppm (intensity ratio ca. 7:3). The former resonance is assigned to **1** and the latter to 1,5-$Se_2S_2N_4$.[48] The ^{77}Se chemical shifts of $(Se_3N_2)^{2+}$, $(Se_2SN_2)^{2+}$, and $(SeS_2N_2)^{2+}$ in SO_2 at −60 °C have been reported as 2434,[18] 2412, and 2422[19] ppm. It is reasonable to expect that the two equivalent selenium atoms in $(Se_2SN_2)^{\bullet+}$ will become more shielded with the addition of one π-electron. While no ^{77}Se NMR spectroscopic data have previously been reported for $(E_3N_2)^{\bullet+}$, Haas et al.[3] have observed that the ^{77}Se chemical shifts of $(Se_2SN_2X)^+$ (X = Cl, Br) with various counterions span a narrow range of 1571−1595 ppm providing indirect support for our assignment.

Vibrational analysis provides further verification for the presence of $[(Se_2SN_2)Cl]_2$ as the main component in the crystalline bulk material. The Raman spectrum of **1** is shown in Figure 3. The five-membered (Se_2SN_2) ring belongs to the point group C_{2v}, and, therefore, all nine fundamental vibrations ($4a_1$, $1a_2$, $1b_1$, $3b_2$**)** are Raman-active. The calculated and observed fundamental vibrations together with the main contributions to their potential energy distributions are given in Table 5. The assignment of the Raman spectrum of **1** based on the potential energy distribution is consistent with those reported for $(Se_xS_{3-x}N_2)^{2+}$,[19,20] when the differences in the bond orders of $(E_3N_2)^{\bullet+}$ and $(E_3N_2)^{2+}$ are taken into account.

Table 6. Comparison of Selected Stretching Force Constants of $Se_2SN_2^{+\bullet}$ and Some Related Species (N m^{-1})

compound	f_{S-N}	$f_{S=N}$	f_{Se-N}	$f_{Se=N}$	f_{Se-Se}	f_{Se-S}	f_{S-S}	ref
$Se_2SN_2^{\bullet+}$		467	197		163			this work
$S_3N_2^{2+}$	333	443					155	20
$SeS_2N_2^{2+}$	363	416	288			212		19
$Se_2SN_2^{2+}$		339		425	197			20, 44
$Se_3N_2^{2+}$			304	375	222			18, 20
$Se_3N_2Cl^+$			220		190			17
S_4N_2	249	476					280	49
SeS_3N_2	286	424				155		49
S_4N_4	376							50
$Se_2S_2N_4$	355		252					11
Se_4N_4			252					11

The two bands at 980 and 951 cm^{-1} are mainly the asymmetric (b_2) and symmetric (a_1) $\nu_{S=N}$ stretching vibrations, respectively, and those at 470 and 359 cm^{-1} are the asymmetric (b_2) and symmetric (a_1) ν_{Se-N} stretching vibrations. The strong band due to the Se−Se stretching vibration (a_1) is observed at 269 cm^{-1}. The bending and torsion modes lie generally at smaller wavenumbers with the exception of the band at 627 cm^{-1} (a_1) for which the δ_{NSN} bend exhibits a significant contribution to the potential energy. The force constants of $Se_2N_2S^{+\bullet}$ are reasonable, as exemplified by data for related species in Table 6.

A strong ESR signal was observed for a powdered sample of $[(Se_2SN_2)Cl]_2$ with $aN = 12.98$ G and $g = 2.0143$ at room temperature indicating the presence of radicals in the solid state. Unfortunately, however, no solution ESR spectra could be obtained due to the slight solubility of the Se-containing system in common solvents (C_7H_8, CH_2Cl_2, $CHCl_3$, or DMSO). We note that the ESR spectrum of the analogous all-sulfur system $[(S_3N_2)Cl]_2$ in SO_2-SOCl_2 at room temperature consists of a 1:2:3:2:1 quintet ($aN = 3.16$ G, $g = 2.0113$).[25] The larger g value for **1** is consistent with the larger spin−orbit coupling contribution of selenium.[51−53]

Conclusions

The products of the reaction between $[(Me_3Si)_2N]_2S$ and $SeCl_4$ is dependent on the reaction conditions. When the reaction is carried out in CS_2 at −70 °C, 1,5-$Se_2S_2N_4$ is the main product. At ambient temperature the reaction mixture contains 25% of ionic $[(Se_2SN_2)Cl]_2$ in addition to 1,5-$Se_2S_2N_4$. In dioxane at slightly elevated temperatures (50 °C) $(Se_2SN_2)_2Cl_2$ is the main product.

Acknowledgment. Financial support from the Academy of Finland and NSERC (Canada) is gratefully acknowledged.

Supporting Information Available: Crystallographic information for $[(Se_2SN_2)Cl]_2$ (**1**) and Se_8 (**2**) in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010141H

---

(46) $Me_3SiN{=}S{=}NSiMe_3$ has been reported to exhibit a ^{14}N resonance at −54.2 ppm.[47]

(47) Habben, C.; Meller, A.; Noltemeyer, M.; Sheldrick, G. M. *J. Organomet. Chem.* **1985**, *288*, 1.

(48) The ^{77}Se chemical shift of 1,5-$Se_2S_2N_4$ in CS_2 is 1418 ppm.[11]

(49) Maaninen, A.; Siivari, J.; Suontamo, R. J.; Konu, J.; Laitinen, R. S.; Chivers, T. *Inorg. Chem.* **1997**, *36*, 2170.

(50) Steudel, R. *Z. Naturforsch.* **1981**, *36a*, 850.

(51) Chandrasekar, V.; Chivers, T.; Kumaravel, S. S.; Parvez, M.; Rao, M. N. S. *Inorg. Chem.* **1991**, *30*, 4125.

(52) Bestari, K.; Cordes, A. W.; Oakley, R. T.; Young, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 2249.

(53) Awere, E.; Passmore, J.; Preston, K. F.; Sutcliffe, L. H. *Can. J. Chem.* ***1988***, 66, 1776.