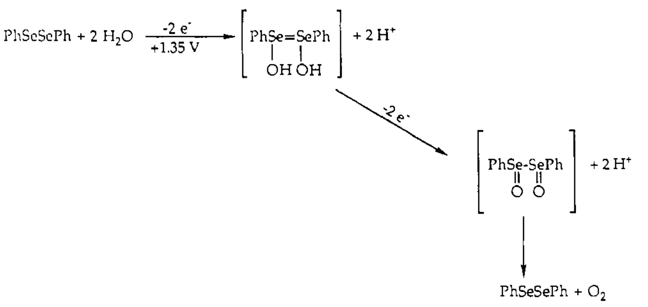
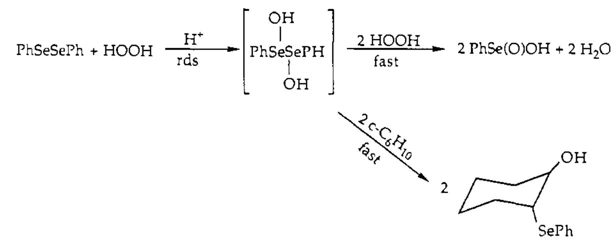
Scheme I. PhSeSePh-Catalyzed Electrooxidation of Water



Scheme II. 1-(PhSe)-2-OH Derivatization of Cyclohexene



V to give PhSeSePh and PhSeH (Table I).

The electrochemical behaviors of PhSeSePh and PhSeH in the presence of $^{-}$OH are similar (Figures (1d and 2b), and the elimination of the reduction peak for PhSeSePh after the addition of 2 equiv of $^{-}$OH indicates that reductive hydrolysis occurs.[20]

$$2\mathrm{PhSeSePh} + 4\,^{-}\mathrm{OH} \rightarrow 3\mathrm{PhSe}^{-} + \mathrm{PhSe(O)O}^{-} + 2\mathrm{H_2O} \qquad (2)$$

Such formation of PhSe$^-$ accounts for the analogous electrochemistry of PhSeSePh and PhSeH in the presence of excess $^{-}$OH. Oxidation of PhSe$^-$ in the presence of excess $^{-}$OH occurs at +0.2 V, and the peak current increases with $^{-}$OH concentration up to a mole ratio of 6:1 (Table I) to give PhSe(O)$_2$O$^-$ as the sole product. Thus, the combination of 12 $^{-}$OH per PhSeSePh is electrooxidized at +0.2 V via a 10-electron process.

$$\mathrm{PhSeSePh} + 12\,^{-}\mathrm{OH} \rightarrow 2\mathrm{PhSe(O)_2O}^{-} + 6\mathrm{H_2O} + 10\mathrm{e}^{-} \qquad (3)$$

Oxidation of PhSeH at +0.9 V yields PhSeSePh and protons, which in combination are reduced at +0.05 V (Table I). In contrast, oxidation of PhSeSePh in the presence of excess water at +1.35 V yields dioxygen. A reasonable mechanistic pathway is outlined in Scheme I.

Scheme II presents plausible reaction pathways for the photolytic- and proton-induced oxygenation of PhSeSePh by HOOH, with formation of the 1:1 adduct being the rate-determining step. This adduct reacts with two more HOOH molecules to form PhSe(O)OH. When excess olefin is present, it reacts with the [PhSe(OH)Se(OH)Ph] adduct to give the 1-(PhSe)-2-OH derivatives of the olefin.

In summary, PhSeSePh is a versatile redox catalyst for the reduction of protons, the oxidation of water, and, in combination with HOOH, the derivatization of olefins. A previous report[7] discusses its utility as a trap for carbon radicals (2R$^\bullet$ + PhSeSePh → 2PhSeR). Much of this parallels the redox chemistry of dioxygen.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-8516247. We are grateful to Professor D. H. R. Barton (of this department) and his associates for their assistance, encouragement, and stimulating discussions.

---

[20] *Organic Selenium Compounds: Their Chemistry and Biology*; Klayman, D. L., Gunther, W. H. H., Eds.; Wiley-Interscience: New York, 1973; p 98.

Contribution from the Department of Chemistry, McMaster University,
1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada

Reactions of S_4N_4 and $S_3N_3Cl_3$ with Selenium Chlorides. The Preparations and Crystal Structures of $SeS_2N_2Cl_2$, $(S_5N_5)(SeCl_5)$, and the Disordered Materials $(Se_xS_{3-x}N_2Cl)(SbCl_6)$

Ronald J. Gillespie,* James P. Kent, and Jeffery F. Sawyer

Received April 26, 1989

The reactions of S_4N_4 with $SeCl_4$ and of $S_3N_3Cl_3$ with Se_2Cl_2 in 1:1 molar ratios in SO_2 as solvent give the crystalline compounds $(S_5N_5)(SeCl_5)$ (**1**) and $SeS_2N_2Cl_2$ (**2**), respectively. Compound **2** is also obtained by the reaction of 2 mol of $S_3N_3Cl_3$ with 3 mol of Se_2Cl_2 in acetonitrile. Orange crystals of **1** are orthorhombic, space group *Pnma*, with $a = 11.252$ (2) Å, $b = 12.075$ (2) Å, $c = 9.987$ (2) Å, $V = 1356.4$ (4) Å^3, and $D_c = 2.38$ g cm^{-3} for $Z = 4$. Red-orange crystals of **2** are monoclinic, space group $P2_1/c$, with $a = 10.447$ (2) Å, $b = 9.259$ (2) Å, $c = 13.529$ (3) Å, $\beta = 105.93$ (2)°, $V = 1258.4$ (4) Å^3, and $D_c = 2.55$ g cm^{-3} for $Z = 4$ (ion pair + molecule). In **1** the pentathiazyl $S_5N_5^+$ cation and square-pyramidal $SeCl_5^-$ anion have crystallographic mirror symmetry and are strongly associated by a short Se–N contact of length 2.794 (5) Å in the sixth coordination site around the selenium. Compound **2** surprisingly contains both a neutral molecule $SeS_2N_2Cl_2$ and an intimate ion pair $SeS_2N_2Cl^+Cl^-$ in the same lattice. In the neutral molecule the Se atom has an AX_4E disphenoidal primary geometry and an overall $AX_4Y'_2E$ distorted-octahedral geometry while the geometry of the Se atom in the ion pair is AX_3Y_3E distorted octahedral. The Se···Cl secondary contacts in this structure are described and discussed. The ^{15}N NMR spectrum of **2** in 100% sulfuric acid has a pair of doublets at $\delta = -51.7$ and -137.8 ppm with $J_{^{15}N-^{15}N} = 5.6$ Hz while the ^{77}Se NMR spectra of natural-abundance and ^{15}N-enriched $SeS_2N_2Cl_2$ have a singlet and a doublet with $J_{^{77}Se-^{15}N} = 117.8$ Hz, respectively, at $\delta = 326.0$ ppm consistent with the formation of the $SeS_2N_2Cl^+$ cation in solution. Further reactions of S_4N_4 with $Se_2Cl_2/SbCl_5$ or $SeCl_4/SbCl_5$ mixtures in SO_2 gave disordered compounds with the general formula $Se_xS_{3-x}N_2Cl^+SbCl_6^-$ (x = 0–3). Some crystallographic data for these compounds are reported.

Introduction

Recently, we reported the characterization of the dimeric thiodiselenazyl cation $Se_4S_2N_4^{2+}$ in the compounds $(Se_4S_2N_4)(MF_6)_2$ (M = As, Sb).[1] Previous workers have reported species that may contain similar or related ring systems from the reactions of S_4N_4, $S_3N_3Cl_3$, or bis[bis(trimethylsilyl)amino]sulfane with selenium halides,[2-7] although none of the products of these re-

---

[1] Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 4053.

[2] Alange, G. G.; Banister, A. J. *J. Inorg. Nucl. Chem.* **1978**, *40*, 203.

[3] Paul, R. C.; Arora, C. L.; Kishore, J.; Malhotra, K. C. *Aust. J. Chem.* **1971**, *24*, 1637.

0020-1669/90/1329-1251$02.50/0 © 1990 American Chemical Society

actions have been characterized with any certainty. We have attempted the preparation of other S–Se–N species by the reaction of S_4N_4 or $S_3N_3Cl_3$ with Se_2Cl_2 or $SeCl_4$ and by the reaction of S_4N_4 with $Se_2Cl_2/SbCl_5$ or $SeCl_4/SbCl_5$ mixtures in SO_2 as solvent. The products of these reactions included an unusual compound containing the neutral molecule $SeS_2N_2Cl_2$ and the related ion pair $SeS_2N_2Cl^+Cl^-$ *in the same crystal lattice*, the compound $(S_5N_5)(SeCl_5)$, and disordered compounds with the general formula $Se_xS_{3-x}N_2Cl^+SbCl_6^-$ (x = 0–3). The characterization of these compounds by X-ray crystallography and $^{77}Se/^{15}N$ NMR, infrared, and Raman spectroscopy is described.

Experimental Section

Reaction vessels, the recording of IR and Raman spectra, and the preparation of S_4N_4 and $S_3N_3Cl_3$ were the same as previously described.[1] All reactions were performed in double-bulb reaction vessels. The ^{15}N NMR spectra were obtained at 25.35 MHz on a Bruker WH-250 spectrometer at McMaster University or at 40.55 MHz on a Bruker WH-400 spectrometer at the University of Guelph (Guelph, Ontario, Canada) in 60–2000 scans (60-s relaxation delay time). Samples of 33% or 99% isotopic composition were contained in thin-walled 10-mm-o.d. (WH-250, WH-400) or 15-mm-o.d. (WH-250) NMR tubes (Wilmad). Solid samples were dissolved in H_2SO_4 (95% or 100%) or SO_2. All samples were run unlocked with the probe temperature held constant at ca. 24 °C. The reference was external 7.1 M aqueous $^{15}NH_4Cl$ (99%), which was calibrated against formamide and nitromethane ($\delta_{^{15}N}$ with respect to 7.1 M aqueous $^{15}NH_4Cl$ = 91.1 and 359.7 ppm, respectively). All chemical shifts are reported with respect to nitromethane as reference. ^{77}Se NMR spectra were recorded at 47.77 and 76.41 MHz on the WH-250 and WH-400 instruments in 70–100K and 1–10K scans, respectively. Samples dissolved in H_2SO_4 or SO_2 in thin-walled 10-mm-o.d. NMR tubes were run unlocked at ca. 24 °C and were referenced to saturated selenous acid.

Reaction of S_4N_4 with $SeCl_4$. Preparation of $(S_5N_5)(SeCl_5)$. Sulfur dioxide (ca. 30 mL) was condensed onto a mixture of S_4N_4 (0.688 g, 3.6 mmol) and $SeCl_4$ (0.800 g, 3.6 mmol) contained in one arm of a double-bulb reaction vessel cooled in liquid nitrogen. When the mixture was warmed to room temperature, a greenish yellow solution and solid were obtained together with unreacted S_4N_4. After 2 h of stirring, the solution and solid were both bright orange. No further changes in color were observed on stirring the mixture overnight. Orange crystals of $(S_5N_5)(SeCl_5)$ (mp 145 °C) were obtained from the filtered solution after slowly removing the solvent. A sample of $(S_5N_5)(SeCl_5)$ enriched to 33% in ^{15}N was prepared as outlined above by using 150 mg (0.81 mmol) of 33%-enriched $S_4{}^{15}N_4$.[8]

Raman spectral data for $(S_5N_5)(SeCl_5)$: 1155 (9), 1031 (6), 915 (1), 724 (2), 672 (5), 617 (44), 540 (2), 531 (4), 462 (15), 381 (41), 364 (2), 334 (1), 312 (11), 305 (8), 279 (100), 255 (35), 224 (10), 207 (51), 176 (49), 163 (30), 142 (11), 121 (7), 108 (8), and 85 (23).

Infrared spectral data for $(S_5N_5)(SeCl_5)$: 1073 (s, vbr), 1000 (w, sh), 920 (s, sh), 908 (s, br), 714 (s), 703 (s), 666 (m, sh), 656 (m), 608 (s), 570 (s, br), 515 (s, br), 405 (s), 384 (vs), 377 (s), 362 (w, sh), 354 (m), 338 (s), and 311 (s).

Far-infrared data for $(S_5N_5)(SeCl_5)$: 275 (s), 260–200 (s, br), 179 (w, sh), 172 (w), 155 (w), 128 (m, sh), and 125 (m).

Reaction of S_4N_4 with Selenium Monochloride. S_4N_4 (0.500 g, 2.7 mmol) and Se_2Cl_2 (0.18 mL, 2.2 mmol) were added to opposite sides of a double-bulb reaction vessel. Sulfur dioxide (ca. 20 mL) was then condensed onto the Se_2Cl_2 and warmed to dissolve the Se_2Cl_2. The S_4N_4 bulb was cooled in liquid nitrogen and the orange-brown SO_2/Se_2Cl_2 solution poured through the frit. The S_4N_4 became black on contact with this solution. During 12 h of stirring, a green-black solid slowly formed from a solution that became greenish yellow in color. No crystalline product was obtained, however, after filtering and concentrating the remaining solution. Anal. Found for the green-black solid: S, 31.92; Se, 38.72; N, 11.30; Cl, 17.64. A 33% ^{15}N-enriched sample of the green precipitate was prepared as outlined above by using 50 mg of enriched $S_4{}^{15}N_4$.[8]

Reaction of $S_3N_3Cl_3$ with Se_2Cl_2—Preparation of $SeS_2N_2Cl_2$. $S_3N_3Cl_3$ (0.638 g, 2.6 mmol) and Se_2Cl_2 (0.21 mL, 2.6 mmol) were transferred to separate sides of a double-bulb reaction vessel. The Se_2Cl_2 was dissolved in SO_2 (ca. 30 mL) to give an orange-brown solution, which was poured through the frit onto the $S_3N_3Cl_3$, which immediately dissolved. Within a few minutes, a reddish brown solution formed containing an orange precipitate. No further color changes were observed after stirring for another 24 h. After the solution was filtered, SO_2 was slowly distilled off, leaving dark red-orange needles of $SeS_2N_2Cl_2$. Anal. Calcd for $SeS_2N_2Cl_2$: Se, 32.63; S, 26.50; N, 11.57; Cl, 29.30. Found: Se, 33.93; S, 26.55; N, 8.96; Cl, 30.60. The above reaction typically gave ca. 830 mg of $SeS_2N_2Cl_2$ (85% yield based on N). The preparation of ^{15}N-enriched $SeS_2N_2Cl_2$ was carried out by the above procedure using 99% enriched $S_3{}^{15}N_3Cl_3$ (180 mg, 0.73 mmol). The compound $SeS_2N_2Cl_2$ was also prepared in a glovebag by dropwise addition of Se_2Cl_2 (0.53 mL, 6.52 mmol) to a stirring solution of $S_3N_3Cl_3$ (1.064 g, 4.35 mmol) in acetonitrile (ca. 60 mL).

X-ray Crystallography

All crystals were selected and sealed in dry Lindemann capillaries in a drybox equipped with a microscope under dry nitrogen. Precession photographs were used to check crystal quality and to obtain preliminary cell and symmetry information. Crystal data and the intensity data collection options used for $SeS_2N_2Cl_2$, $(S_5N_5)(SeCl_5)$, and two crystals of $Se_xS_{3-x}N_2Cl^+SbCl_6^-$ with significantly different cell dimensions are summarized in Table I. Lorentz, polarization, and absorption corrections[9] were applied as indicated. Subsequent averaging of equivalent reflections and the rejection of those that were systematically absent or had F_o = 0.0 resulted in the final numbers of nonzero data shown.

Structures were solved by using direct methods[10] ($SeS_2N_2Cl_2$) or by the use of the Patterson function to locate the Sb or Se atoms followed by cycles of least-squares refinement and Fourier/difference Fourier maps to locate missing atoms. Final atomic positional parameters for all four compounds are given in Table II.

Discussion

From the reaction of S_4N_4 and $SeCl_4$ in a 1:1 mole ratio in benzene solution Paul and co-workers[3] isolated a moisture-sensitive orange solid (mp 185–186 °C) which they proposed to be $S_4N_4SeCl_3{}^+Cl^-$ on the basis of conductance measurements and elemental analysis. Banister and Alange[2] repeated this reaction using a benzene–toluene solvent mixture and obtained a bright yellow solid (mp 127–129 °C). The analytical data for this compound again fitted the $S_4N_4SeCl_4$ stoichiometry, but its infrared spectrum was very similar to that of $(S_5N_5)(AlCl_4)$. We found that on mixing S_4N_4 and $SeCl_4$ in SO_2, the resulting greenish yellow solution slowly turned bright orange and an orange powder precipitated. After the solution was concentrated, an orange crystalline material (mp 145 °C) was obtained, which was shown by X-ray crystallography to be $(S_5N_5)(SeCl_5)$. Elemental analyses of the orange powder, however, were found to agree with the $S_4N_4SeCl_4$ stoichiometry as found in previous investigations (Table III).

Infrared and Raman spectra of the orange precipitate (mp 143–145 °C) were the same as those obtained from the crystalline sample. The Raman spectrum was different from the spectrum of a solid mixture of S_4N_4 and $SeCl_4$ and neither the IR nor the Raman spectrum indicated that this solid was a simple $S_4N_4SeCl_4$ adduct.[2] A UV–visible absorption spectrum of the orange solid also showed absorptions due to the $S_5N_5{}^+$ cation.[12] It is probable that the discrepancy between the $(S_5N_5)(SeCl_5)$ stoichiometry and the results of the elemental analyses was due to some sample

---

(4) Clarke, H. G. Ph.D. Thesis, University of Durham, 1974.

(5) Garcia-Fernandes, H. *C. R. Hebd. Seances Acad. Sci.* **1961**, *2522*, 411.

(6) Banister, A. J.; Padley, J. S. *J. Chem. Soc. A* **1967**, 1437.

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

(8) ^{15}N-enriched $S_3N_3Cl_3$ and S_4N_4 were prepared by using 33% or 95% enriched $^{15}NH_4Cl$ in unpublished procedures developed by Dr. T. Chivers and Dr. R. Oakley of the University of Calgary.

(9) X-Ray 76 System of Crystallographic Programs. Technical Report TR446; Computer Science Center, University of Maryland: College Park, MD, 1976. Sheldrick, G. M. SHELX. Program for Crystal Structure Determination. University of Cambridge, 1976.

(10) In the disordered $Se_xS_{3-x}N_2Cl^+SbCl_6^-$ compounds, the cation in the first data set, when assumed to be $SeS_2N_2Cl^+$, gave R = 0.067 for 2150 reflections (all atoms anisotropic). However, there were some large differences in the thermal parameters of the atoms in the cation, which suggested some substitutional disorder. When the population parameters of the atoms in the cation were refined, the residual significantly improved to R = 0.034. For the data set collected for the crystal from the reaction of S_4N_4 with $SeCl_4$ and $SbCl_5$, the population parameters of the atoms in the cation were again refined and indicated the presence of a much higher concentration of selenium in the positions around the cation.

(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1965.

(12) Zahradnik, R.; Banister, A. J.; Clarke, H. G. *Collect. Czech. Chem. Commun.* **1973**, *38*, 998.

Table I. Crystal Data and Details of Data Collections[a] and Structure Refinements

	$SeS_2N_2Cl_2$[b]	$(S_5N_5)(SeCl_5)$[c]	$Se_xS_{3-x}N_2Cl^+SbCl_6^-$[d,e]
Crystal Data			
system	monoclinic	orthorhombic	monoclinic
a, Å	10.447 (2)	11.252 (2)	7.000 (2), 7.045 (2)
b, Å	9.259 (2)	12.075 (2)	14.294 (4), 14.392 (5)
c, Å	13.529 (3)	9.987 (2)	13.486 (2), 13.489 (3)
β, deg	105.93 (2)		97.52 (1), 97.27 (2)
V, Å^3	1258.4 (4)	1356.4 (4)	1337.8 (5), 1356.8 (6)
Z	4 (ion pair + molecule)	4	4
fw	484.0	486.5	
D_c, g cm^{-3}	2.55	2.38	
μ(Mo K$\bar{\alpha}$), cm^{-1}	77.2	46.6	
space group	$P2_1/c$	$Pnma$	$P2_1/c$
Data Collections and Structure Refinements[f]			
stds (no. interval)	3/47	3/50	3/47, 3/67
scan range	($K\alpha_1$ - 0.85°) to ($K\alpha_2$ + 0.85°)	($K\alpha_1$ - 0.9°) to ($K\alpha_2$ + 0.9°)	($K\alpha_1$ - 0.9°) to ($K\alpha_2$ - 0.9°), ($K\alpha_1$ - 0.9°) to ($K\alpha_2$ + 0.9°)
scan speeds, deg/min	3.5–29.3	2.0–29.3	2.0–29.3, 4.0–29.3
structure solution	direct methods (SHELX)	Patterson	Patterson
abs cor (d in cm)[g]	ABSORB {100}: 0.0105 {010}: 0.0105 $(0\bar{1}1)$, $(01\bar{1})$ 0.0082 8 × 9 × 9 grid A^*: 1.26–1.84	ABSORB {100}: 0.0073 {010}: 0.0025 {101}: 0.0140 8 × 12 × 6 grid A*: 2.52–5.16	spherical, none (irregular shape)
no. of data collcd	3648	3531	4148, 3691
no. of data with			
$F > 6\sigma(F)$	1969	1166	2126, 1909
$F > 2\sigma(F)$	2469	1434	2630, 2444
R-factors			
2σ			
R_1	0.061	0.046	0.046, 0.063
R_2	0.071	0.038	0.042, 0.063
6σ			
R_1	0.047	0.032	0.034, 0.047
R_2	0.062	0.031	0.037, 0.054
max shift/error	0.17	0.01	0.06, 0.30
wt scheme[h]	$(\sigma^2F + 0.0018F^2)^{-1}$	$(\sigma^2F + 0.0043F^2)^{-1}$	$w = xy$,[j] $w = xy$[k]
final ΔF Fourier			
max. peak, e Å^{-3}	1.33	1.06	2.30, 2.49
min. trough, e Å^{-3}	-1.22	-0.73	-0.80, -1.58
programs[9]	X-ray 76 and SHELX on CDC 6900 and CYBER computers		

[a] Syntex $P2_1$ diffractometer; Mo Kα radiation (λ = 0.71069 Å); θ–2θ collection mode; maximum 2θ = 55° in each data collection. [b] Crystals were large dark-green needles although smaller fragments are dark-red in appearance. [c] Crystals were orange and approximately spear-shaped needles. [d] Crystals from reactions $S_4N_4/Se_2Cl_2/SbCl_5$ varied considerably in color from dark yellow to orange to red as well as in crystal forms. [e] Unit cells determined for other crystals:

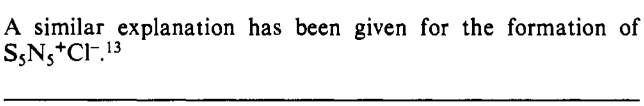
a, Å	b, Å	c, Å	β, deg	V, Å^3
6.978 (2)	14.293 (5)	13.446 (3)	97.62 (2)	1329.2 (7)
7.023 (3)	14.382 (8)	13.428 (5)	97.32 (3)	1345.2 (10)
7.028 (1)	14.379 (2)	13.411 (2)	97.30 (1)	1344.3 (3)

[f] Stationary crystal–stationary counter backgrounds at each end of scan, each for one-fourth of the scan time. Scan speeds were dependent on intensities in 2-s prescans. [g] Lorentz and polarization corrections were applied to all data collected. Absorption corrections were made after the composition of each crystal had been established. [h] In each case the comparison of the $\langle w\Delta F^2\rangle$ as a function of F_o and sin θ after the use of these schemes showed no systematic trends. [i] Neutral-atom scattering curves were taken from ref 11. [j] $x = F/24$ if $F < 24$, or $x = 70/F$ if $F > 70$ and $y = (\sin\theta)/0.23$ if $\sin\theta < 0.23$, and $y = 0.44/(\sin\theta)$ if $\sin\theta > 0.44$, otherwise $x = y = 1.0$. [k] $x = F/32$ if $F < 32$, or $x = 38/F$ if $F > 38$, and $y = (\sin\theta)/0.29$ if $\sin\theta < 0.29$ or $y = 0.34/(\sin\theta)$ if $\sin\theta > 0.34$, otherwise $x = y = 1.0$.

decomposition. Both the crystals and the precipitate rapidly decompose on exposure to the atmosphere. It seems reasonable to conclude that the major product of this reaction is $(S_5N_5)(SeCl_5)$.

Two previous attempts[5,6] have been made to identify the product(s) from the reaction of S_4N_4 and Se_2Cl_2 in a 1:1 mole ratio. This reaction was carried out in SO_2 in an attempt to obtain crystals suitable for X-ray crystallography, but no crystalline material was obtained. Elemental analysis of the green-black solid gave the composition $Se_2S_4N_3Cl_2$, which is not consistent with any of the products reported by earlier workers.[5,6] Presumably, the product was a mixture. Infrared and ^{15}N NMR data showed that an important product of this reaction was the $S_4N_3^+$ cation.

No reaction of selenium(IV) chloride with $S_3N_3Cl_3$ in a 1:1 mole ratio was observed. Presumably, the reaction between S_4N_4 and $SeCl_4$ to give $S_5N_5^+SeCl_5^-$ involves chlorination of S_4N_4 by $SeCl_4$ to give $S_3N_3Cl_3$, $S_4N_4Cl_2$, and NSCl followed by addition of SN^+ to S_4N_4.



A similar explanation has been given for the formation of $S_5N_5^+Cl^-$.[13]

---

(13) Zborilova, L.; Gebauer, P. *Z. Chem.* **1979**, *19*, 32.
(14) Christian, B. H.; Collins, M. J.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1986**, *25*, 777.
(15) Wudl, F.; Zellers, E. T. *J. Am. Chem. Soc.* **1980**, *102*, 5430.

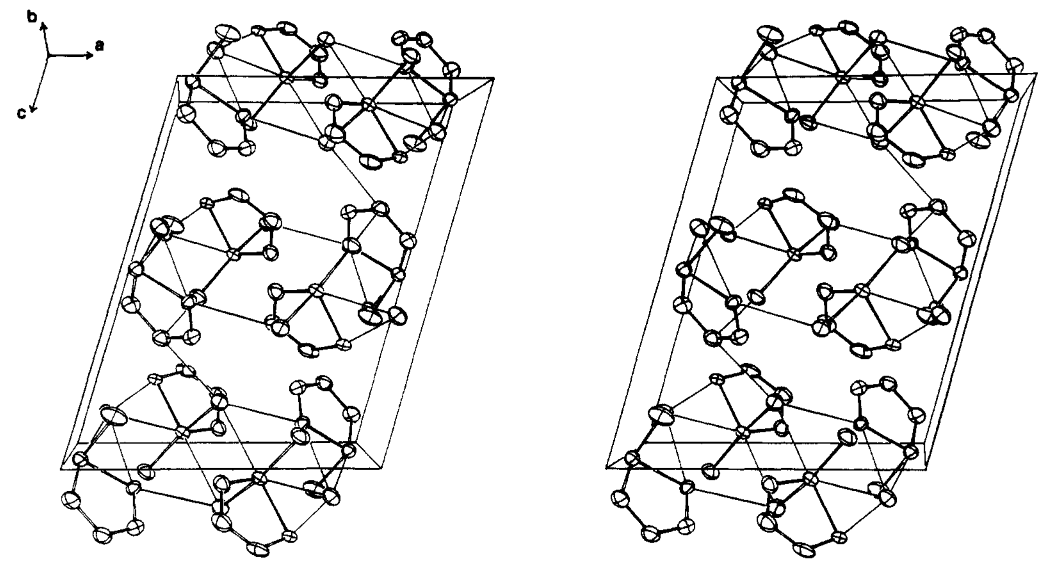


Figure 1. Stereoscopic view (down *b*) of the crystal packing in $SeS_2N_2Cl_2$.

Table II. Final Atomic Positional Parameters (×10^4)

atom	*x*	*y*	*z*
(a) $SeS_2N_2Cl_2$			
Se(1)	444.1 (7)	−2263.2 (8)	4939.0 (6)
Cl(1)	1127 (3)	−3494 (2)	3743 (2)
Cl(2)	843 (2)	367 (2)	3874 (2)
S(1)	2431 (2)	−1256 (2)	5785 (1)
S(2)	1885 (2)	−3724 (2)	6788 (2)
N(1)	2859 (7)	−2464 (8)	6718 (5)
N(2)	576 (7)	−3636 (7)	5891 (5)
Se(2)	3553.8 (7)	1885.6 (8)	4504.8 (5)
Cl(21)	2721 (2)	3299 (2)	5712 (2)
Cl(22)	4467 (2)	39 (2)	3563 (2)
S(3)	2078 (2)	2828 (2)	3059 (1)
S(4)	4496 (2)	4321 (3)	3585 (2)
N(3)	4798 (7)	3194 (7)	4466 (5)
N(4)	3085 (8)	4115 (8)	2864 (5)
(b) $(S_5N_5)(SeCl_5)$			
Se(1)	3343.0 (4)	2500	5953.7 (6)
Cl(1)	1522 (1)	2500	6640 (2)
Cl(2)	2964 (1)	3874 (1)	4265 (1)
Cl(3)	3890 (1)	3920 (1)	7462 (1)
S(1)	1221 (1)	1291 (1)	163 (1)
S(2)	3597 (1)	638 (1)	986 (1)
S(3)	5326 (1)	2500	1582 (2)
N(1)	2522 (3)	1400 (3)	656 (4)
N(2)	4704 (3)	1357 (3)	1369 (4)
N(3)	681 (4)	2500	−12 (5)
(c) $Se_xS_{3-x}N_2Cl^+SbCl_6^-$[a]			
Sb	1575.2 (6)	2706.5 (3)	4794.3 (3)
Cl(1)	−342 (3)	2555 (2)	3230 (1)
Cl(2)	3600 (3)	2877 (1)	6340 (1)
Cl(3)	4284 (3)	2223 (1)	4053 (1)
Cl(4)	−1102 (3)	3181 (2)	5549 (2)
Cl(5)	1002 (4)	1131 (1)	5207 (2)
Cl(6)	2181 (3)	4294 (1)	4431 (1)
Cl(7)	7174 (3)	533 (2)	2907 (2)
X(1)	4332 (2)	4339 (1)	2400 (1)
X(2)	6396 (3)	4150 (2)	1224 (1)
X(3)	8021 (8)	4790 (4)	1835 (5)
X(4)	8098 (3)	4993 (2)	2975 (2)
X(5)	6319 (6)	4542 (3)	3412 (3)

[a] Parameters are from the first data set. Positional parameters for the second data set are given in the supplementary material.

Table III. Analyses of the Precipitate from a Mixture of S_4N_4 and $SeCl_4$

element	% found				% calcd	
	a		*b*	*c*	$(S_5N_5)(SeCl_5)$	$S_4N_4SeCl_4$
S	31.9	31.7	28.71	31.5	33.0	31.7
N	13.3	13.7	13.88	12.8	14.4	13.8
Se	19.8	20.0	20.60		16.2	19.5
Cl	35.4	35.0	34.61	35.03	36.4	35.1

[a] This work. [b] Reference 2. [c] Reference 3.

The reaction of $S_3N_3Cl_3$ and Se_2Cl_2 in $SOCl_2$ solution has been shown by Clarke[4] to give an orange precipitate containing Se. No consistent analyses for this product were obtainable. In the present work, the reaction of equimolar amounts of $S_3N_3Cl_3$ and Se_2Cl_2 in SO_2 gave an orange solid and a reddish brown solution from which a red-orange crystalline material was isolated. X-ray crystallography and elemental analyses showed that the orange-red crystals and the orange solid both had the composition $SeS_2N_2Cl_2$. This product was also isolated when this reaction was carried out in acetonitrile with a 2:3 stoichiometry of $S_3N_3Cl_3$ and Se_2Cl_2. The composition $SeS_2N_2Cl_2$ is identical with that established by Banister and Padley for the product obtained from the reaction of S_4N_4 and Se_2Cl_2 in $SOCl_2$.[6]

Crystal Structures. (a) $SeS_2N_2Cl_2$. Crystals from the reaction of $S_3N_3Cl_3$ and $SeCl_4$ have been shown by X-ray analysis to have the composition $SeS_2N_2Cl_2$. Surprisingly, the asymmetric unit of this compound (Figure 1) contains three distinct species: the molecule $SeS_2N_2Cl_2$, the cation $SeS_2N_2Cl^+$, and a chloride ion Cl^-. However, there is evidence of strong interactions between the $SeS_2N_2Cl^+$ cation and the Cl^- ion, as well as several other significant Se···Cl and S···Cl contacts. As far as we are aware, it is rare to find both molecular and ionic forms of a compound in the same crystal lattice.

The $SeS_2N_2Cl_2$ molecule consists of a planar SeS_2N_2 ring with the two Cl atoms bonded to Se resulting in an AX_4E disphenoidal geometry for that atom (Figure 2). The two Se–Cl bonds [2.431 (3) and 2.474 (3) Å] are significantly longer than the Se–Cl distance in the $SeS_2N_2Cl^+$ cation in the same compound [2.249 (3) Å] and Se–Cl distances in several other compounds containing both 4- and 5-coordinate Se atoms (Tables IV and V). The significant difference in the lengths of the two Se–Cl bonds is due to other charge-transfer interactions involving Cl(21) and Cl(22).

The S–Se bond in the $SeS_2N_2Cl_2$ molecule [2.305 (2) Å] is significantly longer than the sum of the covalent radii (2.21 Å), the S–Se distance of 2.277 (3) Å in the $SeS_2N_2Cl^+$ cation, and the mean (2.247 Å) of the Se–Se (2.351 Å average) and S–S (2.143 Å average) bond lengths in the $Se_4S_4N_4^{2+}$ and $S_6N_4^{2+}$ cations.[1,17] Few other Se–S distances in ring systems have been determined. [The S–Se distance in 1-dioxo-3-formyl-5,8-di-

---

(16) Gawatt, D. G.; Cheng, P. T.; Nyburg, S. C.; Schmid, G. H. *Cryst. Struct. Commun.* **1974**, *3*, 361.

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

Table IV. Bond Lengths (Å), Bond Angles (deg), and Significant Contact Distances with Estimated Deviations in Parentheses for $SeS_2N_2Cl_2$[a]

Bond Lengths			
Ion Pair			
Se(1)-Cl(1)	2.249 (3)	S(1)-Cl(2)	3.056 (3)
Se(1)-S(1)	2.277 (2)	S(1)-Cl(22)^{II}	3.314 (3)
Se(1)-N(2)	1.788 (7)	S(2)-N(1)	1.569 (8)
Se(1)-Cl(2)	2.917 (2)	S(2)-N(2)	1.561 (6)
Se(1)-Cl(2)^{I}	2.941 (2)	S(2)-Cl(21)^{III}	3.343 (3)
Se(1)-Cl(21)^{I}	3.321 (2)	S(2)-Cl(22)^{IV}	3.312 (3)
S(1)-N(1)	1.653 (7)		
Molecule			
Se(2)-Cl(21)	2.433 (3)	Se(2)-Cl(22)^{II}	3.364 (2)
Se(2)-Cl(22)	2.475 (2)	S(3)-N(4)	1.658 (8)
Se(2)-S(3)	2.304 (2)	S(3)-Cl(2)	2.976 (3)
Se(2)-N(3)	1.788 (7)	S(4)-N(3)	1.550 (7)
Se(2)-Cl(2)	3.066 (2)	S(4)-N(4)	1.540 (7)
Bond Angles			
Ion Pairs			
Cl(1)-Se(1)-S(1)	98.29 (9)	N(1)-S(1)-Cl(22)^{II}	89.3 (2)
Cl(1)-Se(1)-N(2)	100.4 (2)	Cl(2)-S(1)-Cl(22)^{II}	108.79 (8)
Cl(1)-Se(1)-Cl(2)	87.22 (8)	N(1)-S(2)-N(2)	111.0 (4)
Cl(1)-Se(1)-Cl(2)^{I}	167.90 (7)	N(1)-S(2)-Cl(21)^{III}	109.6 (3)
Cl(1)-Se(1)-Cl(21)^{I}	98.73 (8)	N(1)-S(2)-Cl(22)^{IV}	84.5 (2)
S(1)-Se(1)-N(2)	92.9 (2)	N(2)-S(2)-Cl(21)^{III}	89.0 (3)
S(1)-Se(1)-Cl(2)	70.86 (6)	N(2)-S(2)-Cl(22)^{IV}	161.4 (3)
S(1)-Se(1)-Cl(2)^{I}	88.35 (7)	Cl(21)^{III}-S(2)-Cl(22)^{IV}	75.79 (7)
S(1)-Se(1)-Cl(21)^{I}	162.84 (7)	S(1)-N(1)-S(2)	120.4 (4)
N(2)-Se(1)-Cl(2)	163.0 (2)	Se(1)-N(2)-S(2)	118.3 (4)
N(2)-Se(1)-Cl(2)^{I}	89.3 (2)	Se(2)-Cl(21)-S(2)^{V}	156.9 (1)
N(2)-Se(1)-Cl(21)^{I}	81.9 (2)	Se(2)-Cl(21)-Se(1)^{I}	100.38 (7)
Cl(2)-Se(1)-Cl(2)^{I}	85.40 (6)	S(2)^{V}-Cl(21)-Se(1)^{I}	84.68 (7)
Cl(2)-Se(1)-Cl(21)^{I}	112.14 (6)	Se(2)-Cl(22)-S(1)^{II}	96.59 (7)
Cl(2)^{I}-Se(1)-Cl(21)^{I}	75.31 (6)	Se(2)-Cl(22)-Se(2)^{II}	101.98 (7)
Se(1)-S(1)-N(1)	97.2 (2)	Se(2)-Cl(22)-S(2)^{IV}	105.91 (8)
Se(1)-S(1)-Cl(2)	64.40 (6)	S(1)^{II}-Cl(22)-Se(2)^{II}	68.66 (5)
Se(1)-S(1)-Cl(22)^{II}	164.37 (9)	S(1)-Cl(22)-S(2)^{IV}	149.37 (9)
N(1)-S(1)-Cl(2)	161.6 (2)	Se(2)^{II}-Cl(22)-S(2)^{IV}	125.08 (8)
Molecule			
Cl(21)-Se(2)-Cl(22)	167.64 (8)	Se(2)-S(3)-Cl(2)	69.67 (6)
Cl(21)-Se(2)-S(3)	95.00 (7)	N(4)-S(3)-Cl(2)	165.5 (2)
Cl(21)-Se(2)-N(3)	93.0 (2)	N(3)-S(4)-N(4)	111.1 (4)
Cl(21)-Se(2)-Cl(2)	87.71 (7)	Se(2)-N(3)-S(4)	118.9 (4)
Cl(21)-Se(2)-Cl(22)^{II}	91.15 (6)	Se(3)-N(4)-S(4)	121.8 (4)
Cl(22)-Se(2)-S(3)	95.00 (7)	Se(1)-Cl(2)-S(1)	44.73 (5)
Cl(22)-Se(2)-N(3)	93.8 (2)	Se(1)-Cl(2)-Se(2)	119.47 (6)
Cl(22)-Se(2)-Cl(2)	89.83 (7)	Se(1)-Cl(2)-S(3)	163.27 (8)
Cl(22)-Se(2)-Cl(22)^{II}	78.02 (6)	Se(1)-Cl(2)-Se(1)^{I}	94.58 (7)
S(3)-Se(2)-N(3)	92.3 (2)	S(1)-Cl(2)-Se(2)	75.22 (6)
S(3)-Se(2)-Cl(2)	65.53 (6)	S(1)-Cl(2)-S(3)	120.04 (8)
S(3)-Se(2)-Cl(22)^{II}	170.27 (7)	S(1)-Cl(2)-Se(1)^{I}	93.17 (7)
N(3)-Se(2)-Cl(2)	157.8 (2)	Se(2)-Cl(2)-S(3)	44.18 (4)
N(3)-Se(2)-Cl(22)^{II}	94.9 (2)	Se(2)-Cl(2)-Se(1)^{I}	95.77 (6)
Cl(2)-Se(2)-Cl(22)^{II}	107.30 (6)	S(3)-Cl(2)-Se(1)^{I}	93.19 (7)
Se(2)-S(3)-N(4)	95.8 (2)		

[a] Symmetry transformations: I, $-x, -y, 1 - z$; II, $1 - x, -y, 1 - z$; III, $x, -1 + y, z$; IV, $x, -^1/_2 - y, ^1/_2 + z$; V, $x, 1 + y, z$.

methyl-1,2-dihydro-1-thia-2-selenanaphthalene is 2.205 (1) Å; that in bis(*o*-nitrobenzeneselenyl) sulfide is 2.202 (2) Å.[18,19]]

The Se–N bond length in $SeS_2N_2Cl_2$ [1.789 (7) Å] is the same as the Se–N bond lengths in the $SeS_2N_2Cl^+$ cation [1.789 (7) Å] and is slightly longer than the Se–N bonds in the $Se_4S_2N_4^{2+}$ cation [1.75–1.76 (1) Å]. Somewhat shorter bonds [1.680 (4)–1.787 (6) Å] have been observed in a series of molecules in which various cyclic and acyclic resonance forms contribute.[20] In these latter molecules, when Se^{IV} type resonance structures are predominant, the crystal packing and overall environments of the Se atoms are completed by Se⋯Cl distances of 2.595 (2) (×2), 2.634 (2), and 2.983 (2) Å.[20] All the above Se–N bonds have some Se=N double bond character as they are somewhat shorter than the sum of the covalent radii and Se-N single bond lengths of ca. 1.82–1.85 Å in acyclic compounds. Other Se-N bond lengths have been summarized.[1,21] Similarly, S-N bond lengths in the $SeS_2N_2Cl_2$ molecule and the $SeS_2N_2Cl^+$ cation are not significantly different and are comparable to distances in other SN cations such as $S_4N_4^{2+}$ and $S_5N_5^+$.[22-25]

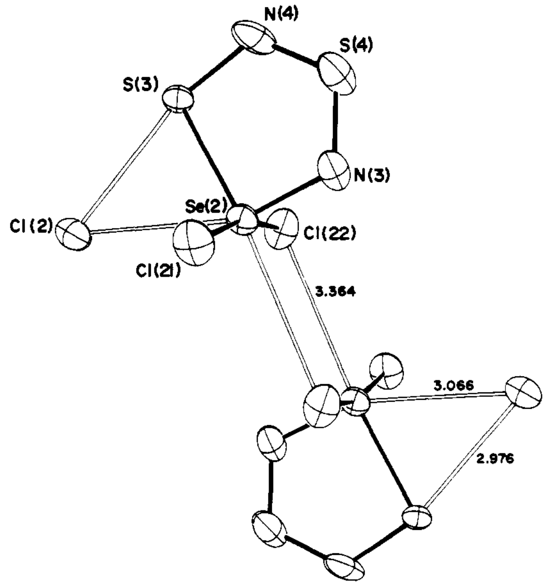


Figure 2. View of a pair of $SeS_2N_2Cl_2$ molecules across a center of symmetry showing the principal Se⋯Cl and S⋯Cl contacts.

Table V. Selected Se–Cl/Se⋯Cl Bond/Contact Distances

compd	Se–Cl/Se⋯Cl dist,[a] Å
$Se_2S_2N_2Cl_2$[b]	2.433 (3), 2.475 (2), 3.066 (2), 3.364 (2)
$SeS_2N_2Cl^+Cl^-$[b]	2.249 (3), 2.941 (2), 2.917 (2), 3.321 (2)
$(S_5N_5)(SeCl_5)$[b]	2.159 (1), 2.364 (1) (×2), 2.404 (1) (×2)
α-$SeCl_4$[c]	2.146 [2.874], 2.166 [2.766] 2.160 [2.924], 2.174 (×3) [2.820 (×3)]; $\sigma \sim 0.005$
β-$SeCl_4$[c]	2.169 [2.766], 2.156 [2.791] 2.186 [2.761], 2.169 [2.769] 2.150 [2.818], 2.150 [2.859]; $\sigma \sim 0.005$
$SeCl_3^+AlCl_4^-$[c]	2.07–2.13 (1) [2.97–3.05 (1)]
$SeCl_3^+MoOCl_4^-$[c]	2.146 [2.883], 2.149 [2.909] 2.150 [2.891]; $\sigma \sim 0.002$
$SeCl_3^+SbCl_6^-$[c]	2.09 (×3) [3.14 (×3)], 2.10 (×3) [3.12 (×3)]; $\sigma \sim 0.01$
1,1-dichloro-2,5-bis((chlorothio)imino)-3,4-dicyanoselenophene[d]	2.369 (1) (×2), 3.29 (×2)
2-(1-chloropropyl)-1,4′-ditolyl selenide dichloride[e]	2.40 (1)
1-chloro-3,5-diphenyl-1,2,4,6-selenatriazine[f]	2.349 (3) [3.444]

[a] Trans-related distances in brackets. [b] This work. [c] Reference 14 and references therein. [d] Reference 15. [e] Reference 16. [f] Oakley, R. T.; Reed, R. W.; Cordes, A. W.; Craig, S. L.; Graham, J. B. *J. Am. Chem. Soc.* **1987**, *109*, 7745.

In $SeS_2N_2Cl_2$ the axial Cl-Se-Cl angle is 167.65 (8)° with the Se-Cl bonds bent away from the ring (S-Se-Cl and N-Se-Cl angles are 93-95°). The equatorial S-Se-N angle [92.4 (2)°] is smaller than the ideal angle of 120° expected for a AX_4E disphenoidal geometry, presumably because this angle is part of

---

(18) Michel, A.; Durant, F. *Cryst. Struct. Commun.* **1980**, *9*, 219.

(19) Eriksen, R. *Acta Chem. Scand.* **1975**, *A29*, 517.

(20) Roesky, H. W.; Weber, K.-L.; Seseke, U.; Pinkert, W.; Noltemeyer, M.; Clegg, W.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1985**, *565*.

(21) Gieren, A.; Lamm, V.; Haddon, R. C.; Kaplan, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 5070.

(22) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F.; Slim, D. R.; Tyrer, J. D. *Inorg. Chem.* **1981**, *20*, 3799.

(23) Gillespie, R. J.; Sawyer, J. F.; Slim, D. R.; Tyrer, J. D. *Inorg. Chem.* **1982**, *21*, 1296.

(24) Fenske, D.; Berg, A.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, *527*, 105.

(25) Berg, A.; Dehnicke, K.; Fenske, D. *Z. Anorg. Allg. Chem.* **1985**, *527*, 111.

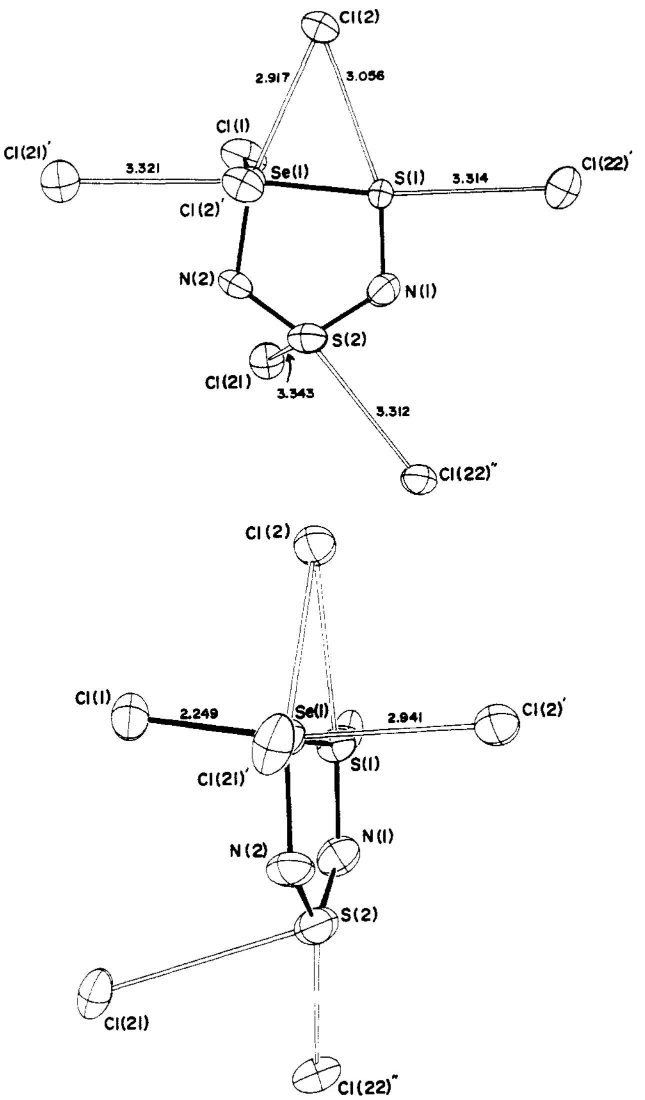


Figure 3. Two views of the $SeS_2N_2Cl^+Cl^-$ ion pair showing principal Se⋯Cl and S⋯Cl contacts.

a five-membered ring, the Se–S bond is long and weak, and there are two additional Se⋯Cl secondary bonds in the same plane of lengths 3.065 (2) and 3.365 (2) Å. These two secondary bonds are approximately colinear with the S–Se and Se–N primary bonds [S–Se–Cl and N–Se–Cl angles are 170.27 (7) and 157.8 (2)°, respectively]. These interactions are 0.73 and 0.53 Å, respectively, less than the van der Waals distance (3.80 Å). In comparison, the axial Cl–Se–Cl angle in 1,1 dichloro-2,5-bis[(chlorothio)imino]-3,4-dicyanoselenophene is 173.46 (5)° with the Cl atoms bending in toward the selenophene ring.[15] In this compound two intramolecular Se⋯Cl contacts of lengths 3.29 Å (×2) virtually in the equatorial plane complete the Se geometry. Overall the geometries of this atom and of Se(2) in $SeS_2N_2Cl_2$ may be described as $AX_4Y'_2E$.[26] As a result of the short Se(2)⋯Cl(22) interaction, pairs of $SeS_2N_2Cl_2$ molecules are linked across centers of symmetry (Figure 2).

Table VI. Equations of Least-Squares Mean Planes of the $S_5N_5^+$ Ring and Equatorial Chlorine Atoms in $SeCl_5^-$ [a]

	$S_5N_5^+$ plane of ring	$SeCl_5^-$ plane of equatorial chlorine atoms
eq of plane[b]	$0.2915\mathbf{I} + 0.9566\mathbf{K} = 6.647$	$0.9506\mathbf{I} - 0.3104\mathbf{K} = 1.847$
atoms and dev, Å	N(2)*, N′(2)*, N(3)*, and S(3)* = 0.004 S(1)* and S′(1)* = 0.014 S(2)* and S′(2)* = 0.008 N(1)* and N′(1)* = 0.030 Se(1) = 0.014	Cl(2)*, Cl′(2)*, Cl(3)*, and Cl′(3)* = 0.004 Se(1) = −0.12

[a] Atoms defining each plane are marked with an asterisk. Primed atoms are related to unprimed atoms by the symmetry transformation x, $^1/_2 - y$, z. [b] Defined in orthogonal angstrom space, i.e., three orthogonal unit vectors **I**, **J**, **K** with **I** parallel to a, **K** perpendicular to a in the plane ac and **J** perpendicular to the plane of ac.

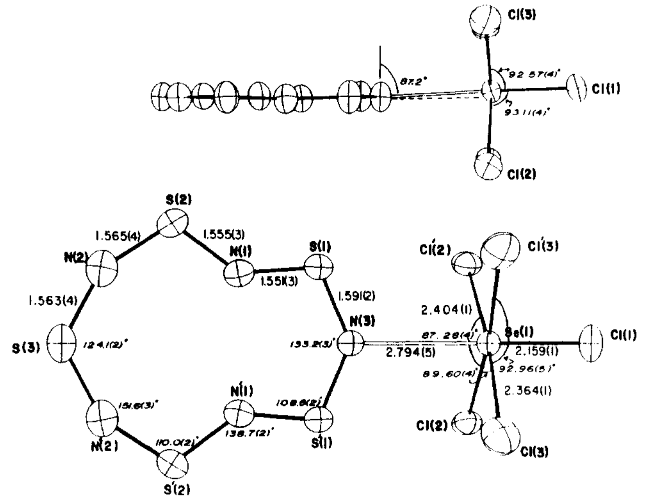


Figure 4. ORTEP diagrams of $(S_5N_5)(SeCl_5)$ showing bond lengths (Å) and bond angles (deg). The N⋯Se contact is shown as an unfilled line.

The $SeS_2N_2Cl^+$ cation is a distorted version of the $SeS_2N_2Cl_2$ molecule, and bond lengths and bond angles are very comparable with the exception of the Se–S and Se–Cl bond lengths and the angles at Se and S (Figure 3, Table V). As with $S_3N_2Cl^+Cl^-$ [27] and $S_3N_2Cl^+FeCl_4^-$,[28] several Se⋯Cl and S⋯Cl anion–cation contacts are significantly less than the van der Waals distances. There are two main interactions. First, the chloride ion Cl(2) bridges the Se–S bond of the cation with Se⋯Cl and S⋯Cl interactions 2.917 (2) and 3.056 (2) Å, respectively, that is, 0.88 and 0.59 Å shorter than the respective van der Waals distances (Se + Cl = 3.80 Å; S + Cl = 3.65 Å). Very similar bridging interactions are a feature of the crystal packings of the cations $S_3N_2^+$, $S_6N_4^{2+}$, $S_4N_3^+$, and $Se_4S_2N_4^{2+}$ as well as $S_3N_2Cl_2$.[1,17,27,28] Second, there is a Se⋯Cl interaction [2.942 (2) Å] approximately colinear with the Se(1)–Cl(1) bond of the cation [Cl(1)–Se(1)⋯Cl(2) = 167.90 (7)°]. With these interactions included, the overall environment of Se(1) is a distorted version of the $AX_4Y'_2E$ geometry of Se(2) (Figure 3) and is very similar to the distorted-octahedral AX_3Y_3E geometries observed for the $SeCl_3^+$ cation[14] (see Table V). As one of the A⋯Y contacts in the AX_3Y_3E geometry of Se(1) shortens, the lone pair E would be expected to be pushed off the pseudo-3-fold axis of the AX_3E triangular pyramid, and the proposed charge-transfer interaction would lengthen the A–X bond trans to the A⋯Y interaction. Eventually, the lone pair would be expected to occupy the equatorial site of a trigonal bipyramidal arrangement of five electron pairs with the two remaining A⋯Y′ contacts bridging equatorial edges of the bipyramid as observed for Se(2). A few other short S⋯Cl contacts (Table V) may be described in a manner similar to the interactions observed in the examples of the $S_3N_2^+$ and $S_6N_4^{2+}$ cations.[17]

Due to the interactions of the chloride ion Cl(2) with S–Se bonds in both the cation and the neutral molecule, the angle between the molecular planes of both the cation and the molecule is very small (5°) (Figure 1). Similar packing arrangements for halide ions are found in some TSeT (TSeT = tetraselenotetracene) compounds such as $(TSeT)_2^+Cl^-$ and $(TSeT)_2^+I^-$.[29,30]

---

(26) Sawyer, J. F.; Gillespie, R. J. *Prog. Inorg. Chem.* **1986**, *34*, 65.
(27) Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Inorg. Chem.* **1966**, *5*, 1767.
(28) Shearer, H. M. M.; Banister, A. J.; Halfpenny, J.; Whitehead, G. *Polyhedron* **1983**, *2*, 149.
(29) Shibeava, R. P.; Kaminskii, V. F. *Kristallografiya* **1978**, *23*, 1183.

Table VII. Bond Lengths (A), Bond Angles (deg), and Significant Contact Distances with Estimated Standard Deviations in Parentheses for the Disordered Compound $Se_xS_{3-x}N_2Cl^+SbCl_6^-$ (I, First Data Set; II, Second Data Set)

Bond Lengths

	I	II		I	II
X(1)–X(2)	2.284 (2)	2.316 (3)	Sb–Cl(1)	2.357 (2)	2.369 (3)
X(1)–X(5)	1.866 (4)	1.927 (6)	Sb–Cl(2)	2.375 (2)	2.379 (3)
X(1)–Cl	2.142 (2)	2.171 (3)	Sb–Cl(3)	2.360 (2)	2.367 (3)
X(2)–X(3)	1.599 (6)	1.596 (10)	Sb–Cl(4)	2.347 (2)	2.350 (4)
X(3)–X(4)	1.562 (7)	1.580 (12)	Sb–Cl(5)	2.366 (2)	2.377 (3)
X(4)–X(5)	1.583 (5)	1.573 (8)	Sb–Cl(6)	2.370 (2)	2.380 (3)

Bond Angles

	I	II		I	II
X(2)–X(1)–X(5)	92.5 (2)	91.1 (2)	Cl(1)–Sb–Cl(2)	177.92 (8)	177.9 (1)
X(2)–X(1)–Cl	104.7 (1)	105.2 (1)	Cl(1)–Sb–Cl(3)	89.31 (7)	89.2 (1)
Cl–X(1)–X(5)	104.0 (2)	104.7 (2)	Cl(1)–Sb–Cl(4)	91.25 (7)	91.4 (1)
X(1)–X(2)–X(3)	94.7 (2)	94.7 (4)	Cl(1)–Sb–Cl(5)	91.61 (8)	91.4 (1)
X(2)–X(3)–X(4)	123.0 (4)	123.7 (7)	Cl(1)–Sb–Cl(6)	89.97 (7)	90.0 (1)
X(3)–X(4)–X(5)	111.2 (3)	111.4 (5)	Cl(2)–Sb–Cl(3)	88.97 (7)	89.1 (1)
X(4)–X(5)–X(1)	111.8 (3)	111.2 (4)	Cl(2)–Sb–Cl(4)	90.48 (7)	90.3 (1)
			Cl(2)–Sb–Cl(5)	89.55 (7)	89.9 (1)
			Cl(2)–Sb–Cl(6)	88.89 (6)	88.7 (1)
			Cl(3)–Sb–Cl(4)	179.36 (7)	179.3 (1)
			Cl(3)–Sb–Cl(5)	89.52 (8)	89.6 (1)
			Cl(3)–Sb–Cl(6)	91.00 (7)	90.9 (1)
			Cl(4)–Sb–Cl(5)	90.15 (9)	90.1 (1)
			Cl(4)–Sb–Cl(6)	89.31 (8)	89.4 (1)
			Cl(5)–Sb–Cl(6)	178.34 (7)	178.5 (1)

Contact Distances (X···Cl < 3.70 Å)[a]

	I	II		I	II		I	II
X(1)···Cl(3)	3.646 (2)	3.642 (3)	X(2)···Cl(7)^{II}	3.504 (3)	3.566 (5)	X(4)···Cl(1)^{IV}	3.654 (3)	3.665 (5)
X(1)···Cl(6)	3.296 (2)	3.290 (3)	X(2)···Cl(5)^{III}	3.687 (3)	3.695 (5)	X(4)···Cl(6)^{IV}	3.398 (3)	3.424 (5)
X(1)···Cl(2)^{I}	3.357 (2)	3.379 (3)	X(2)···Cl(2)^{I}	3.512 (3)	3.548 (4)	X(4)···Cl(2)^{V}	3.439 (3)	3.455 (5)
X(1)···Cl(5)^{I}	3.560 (2)	3.533 (4)	X(2)···Cl(3)^{I}	3.671 (3)	3.677 (4)	X(4)···Cl(6)^{V}	3.673 (3)	3.695 (5)

[a] Sum of van der Waals radii: Se + Cl, 3.80 Å; S + Cl, 3.65 Å. [b] Symmetry transformations: I, x, $^1/_2 - y$, $-^1/_2 + z$; II, $1 - x$, $^1/_2 + y$, $^1/_2 - z$; III, $1 + x$, $^1/_2 - y$, $-^1/_2 + z$; IV, $1 - x$, y, z; V, $1 - x$, $1 - y$, $1 - z$.

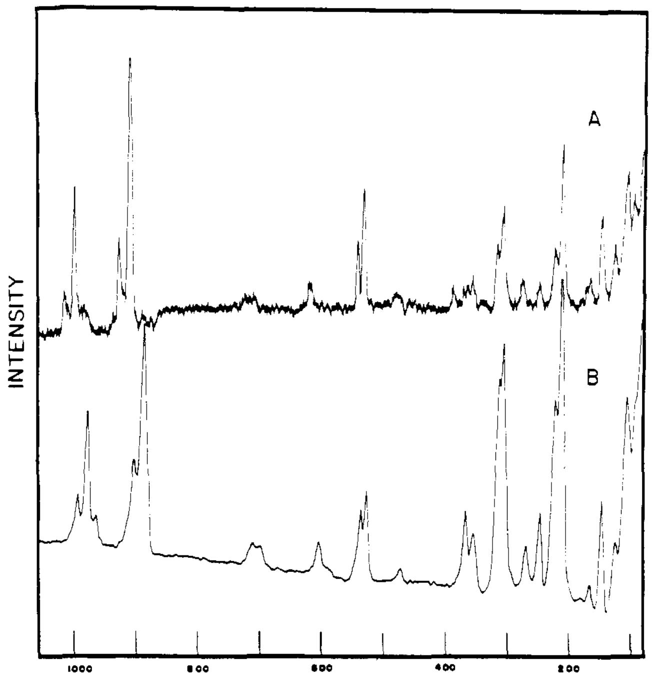


Figure 5. Raman spectra of (A) $SeS_2N_2Cl_2$ at −196 °C and (B) $SeS_2{}^{15}N_2Cl_2$ at room temperature on a spinning sample.

(b) $(S_5N_5)(SeCl_5)$. Crystals obtained from the reaction of equimolar amounts of S_4N_4 and $SeCl_4$ in SO_2 have the composition $(S_5N_5)(SeCl_5)$ and contain the novel pentachloroselenate(IV) anion and a planar azulene-shaped $S_5N_5^+$ ring with crystallographic mirror symmetry (Table VI). The dimensions of the $S_5N_5^+$ cation (Figure 4) are virtually the same as those found for other $S_5N_5^+$ salts.[23,25,31-35] Both $(S_5N_5)(AlCl_4)$ and $(S_5N_5)(SbCl_6)$ contain disordered $S_5N_5^+$ cations[23,33] with a heart shape and an intermediate heart–azulene shape, respectively.

The pentachloroselenate(IV) anion has a square-pyramidal structure, as expected on the basis of VSEPR theory.[36] The Se–Cl bonds in the base of the pyramid [2.404 (1) and 2.364 (1) Å] are longer than the axial Se–Cl bond [2.159 (1) Å] and are comparable to those in $SeCl_6^{2-}$ salts (average 2.40 Å).[37] The Se atom in the $SeCl_5^-$ anion is displaced 0.12 Å out of the plane formed by the four basal Cl atoms toward the apical Cl atom, and hence the Cl_{ax}–Se–Cl_{eq} angles are >90° although these angles would be expected to be less than 90° as is observed in the isoelectronic anion $SbCl_5^{2-}$ in $(S_4N_3)_2(SbCl_5)$[38] and $(NH_4)_2(SbCl_5)$.[39] A similar displacement of the Se atom above the base of the square pyramid is observed in a number of complexes involving seleninyl dichloride, $SeOCl_2{\cdot}XY$ (where the coordinating atoms are Cl, O, or N atoms of $SbCl_5$, $SnCl_4$, $NMe_4{}^+Cl^-$, Ph_3PO, pyridine, 8-hydroxyquinolinium, 2-aminopyridinium, and 2,2′-dipyridinium).[40]

---

(30) Hilti, B.; Mayer, C. W.; Rihs, G. *Helv. Chim. Acta* **1978**, *61*, 1462.
(31) Banister, A. J.; Durrant, J. A.; Rayment, I.; Shearer, H. M. M. *J. Chem. Soc., Dalton Trans.* **1976**, *929*.
(32) Roesky, H. W.; Bowing, W. G. *J. Chem. Soc., Chem. Commun.* **1975**, 735.
(33) Hazell, A. C.; Hazell, R. G. *Acta Chem. Scand.* **1972**, *26*, 1987.
(34) Klinzing, P.; Willing, W.; Muller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, *529*, 35.
(35) Banister, A. J.; Hauptman, Z. V.; Kendrick, A. G.; Small, R. W. H. *J. Chem. Soc., Dalton Trans.* **1987**, *915*.
(36) Gillespie, R. J. *Molecular Geometry*; Van Nostrand-Reinhold: London, 1972.
(37) Engel, G. *Z. Kristallogr., Kristallogeom., Kristallphys., Kristallchem.* **1935**, *90*, 341. Abriel, W. *Acta Crystallogr., Sect. C* **1986**, *C42*, 1113.
(38) Kruss, B.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1972**, *388*, 158.
(39) Webster, M.; Keats, S. *J. Chem. Soc. A* **1971**, 298. Edstrand, M.; Inge, M.; Ingri, N. *Acta Chem. Scand.* **1955**, *9*, 122.

Table VIII. Vibrational Data (cm^{-1}) for $SeS_2N_2Cl_2$ and $S_3N_2Cl_2$[a-c]

$SeS_2N_2Cl_2$		$SeS_2{}^{15}N_2Cl_2$[d]		$S_3N_2Cl_2$	$S_3{}^{15}N_2Cl_2$[d]	
Raman	infrared	Raman	Δ[e]	Raman	Raman	Δ[e]
	1155 (w)					
1017 (8)		999 (13)	18	1018 (33)	997 (21)	21
1002 (33)		979 (44)	23			
985 (6)	975 (m)	966 (4)	19			
				935 (7, sh)		
928 (23)	925 (s)	906 (38)	22	929 (11)	908 (9)	27, 21
908 (100)	908 (s)	893 (84)	15			
	847 (w, sh)					
728 (3)		714 (5)	14	728 (19)	713 (10)	15
718 (3)	718 (s)	698 (5)	20			
	702 (s)					
617 (7)	616 (s, sh)	608 (9)	9			
	608 (vs)					
	589 (s, sh)					
	578 (s)			580 (9)	574 (4)	6
539 (15)		529 (22)	10			
528 (30)	513 (m)	518 (28)	10			
478 (3)	506 (m)	473 (4)	5	459 (2)	453 (2)	6
				406 (38)	397 (32)	9
385 (6)	381 (w)		?	389 (4)	389 (1)	
369 (3)		369 (23)		371 (25)	367 (17)	4
359 (2)	356 (vs)					
354 (4)	347 (vs, sh)	351 (19)	3	349 (23)	343 (15)	6
	339 (s)					
315 (21, sh)		315 (50, sh)				
308 (38)	297 (s)	308 (76)				
270 (9)	287 (s, sh)	270 (12)				
245 (7)	256 (m)	245 (16)		259 (74)	256 (63)	3
223 (16)		222 (51)	1			
211 (43)		211 (100)				
170 (8)		170 (4)		172 (60)	172 (43)	
				155 (5)	155 (3)	
147 (23)		147 (29)		142 (100)	142 (100)	
125 (10)		125 (18)		127 (16)	127 (7)	
				118 (51)	118 (37)	
107 (6)		107 (31)		112 (33)	112 (24)	
91 (w, sh)		91 (w, sh)		86 (29)	86 (25)	
				68 (5)	68 (3)	
				52 (14)	52 (10)	

[a] Raman intensities are given in parentheses. [b] Infrared spectra were recorded on a Perkin-Elmer spectrometer (1400–200 cm^{-1}) and a Nicolet FT-IR system (440–300 cm^{-1}). [c] Infrared spectrum of $S_3N_2Cl_2$ (this work and ref 4) contains strong bands at 1015, 936 (vs), 720, 582, 458, and 500 (br) cm^{-1}. Lit. IR for $S_3N_2Cl_2$: 964 (s), 944 (vs), 745 (w), 716 (sh, s), 708 (vs), 699 (sh, s), 588 (s), 569 (w), 456 (w), and 431 (m) cm^{-1}. [d] Isotopically enriched to 99% in ^{15}N. [e] The isotopic shift $\Delta = \nu(Se_xS_{3-x}{}^{14}N_2Cl_2) - \nu(Se_xS_{3-x}{}^{15}N_2Cl_2)$ (cm^{-1}) of the Raman bands (x = 0 or 1).

In these and similar structures,[15,21,41] there is approximate octahedral geometry around the selenium atom although some of the bond lengths involved are much longer than the primary bond lengths.

In $(S_5N_5)(SeCl_5)$, there is a Se···N contact with a length of 2.794 (5) Å in the direction of the vacant six-coordinate site of the $SeCl_5^-$ ion that, according to the VSEPR model, is occupied by the lone pair. This contact is approximately 0.1 Å shorter than the shortest previously recorded Se···N contact (2.898 Å)[21] and is much shorter than the sum of the van der Waals radii although considerably longer than the sum of the covalent radii of selenium and nitrogen (1.87 Å). It appears that the lone pair in these Se(IV) compounds has a reduced stereochemical activity, and they are probably better regarded as octahedral AX_6E complexes like the $SeCl_6^{2-}$ ion, which has a regular octahedral structure but with unusually long bonds, which is attributed to the lone pair occupying a spherical s orbital. The four equatorial Se–Cl bonds in $(SeCl_5\cdots N)^-$ are then bent away from the axial Se–Cl bond toward the weaker Se···N bond. The crystal packing in $(S_5N_5)(SeCl_5)$ is similar to that found in $(NH_4)_2(SbCl_5)$[39] but differs from that in $(S_4N_3)_2(SbCl_5)$, in which rows of $SbCl_5^{2-}$ ions aligned parallel to the *c* axis are linked by an intermolecular contact between the axial Cl atom of one molecule and the central Sb atom of another molecule in a "head-to-tail" fashion.[38] Two other interionic contacts in $(S_5N_5)(SeCl_5)$ from the atom Cl(2) to S(1) and S(2) [3.188 (2) and 3.252 (2) Å, respectively] are shorter than similar contacts in $(S_5N_5)(SbCl_6)$ [3.468 (7) and 3.309 (7) Å][23] and $(S_5N_5)(AlCl_4)$ [3.493 (3) and 3.495 (3) Å][33] but are comparable to the shortest contacts observed in $(S_5N_5^+)Cl^-$ [3.148 (1)–3.279 (1) Å].[35] In all cases the shortest S···Cl contacts are to the two S atoms that form the reentrant angle at N in each $S_5N_5^+$ ring.

(c) $Se_xS_{3-x}N_2Cl^+SbCl_6^-$. Crystals from the reactions between $S_4N_4/SbCl_5$ and either $SeCl_4$ or Se_2Cl_2 have variable cell parameters, and data sets were collected on two crystals close to the extremes in cell dimensions (Table I). Both structures contained $SbCl_6^-$ anions and disordered cations. It was assumed that the exocyclic atom in each cation was Cl and that the disordered sites in each ring were Se, S, or N before refining the population parameters. These calculations indicated that the disordered cation in the compound from the reaction with $SeCl_4$ has significantly more electron density at each averaged site. Both crystals thus contain varying and different amounts of the disordered cations $Se_xS_{3-x}N_2Cl^+$ (x = 0–3). From a very simplified model of the disorder based on the $S_3N_2Cl^+$ cation and the Se–S-bonded $SeS_2N_2Cl^+$ cation only, the relative amounts of these cations present could be obtained from the compositions of the three-coordinate X(1) site which is 48.7% Se (51.9% S) for the first data set and 77.5% Se (22.5% S) for the second data set (supplementary material). The average bond lengths and bond angles in the two disordered cations are also consistent with the higher Se content of the X(1) site for the second data set. The $SbCl_6^-$ anions in both refinements are approximately octahedral with

---

(40) Hermodsson, Y.; *Ark. Kemi* **1970**, *31*, 199.

(41) Kniep, R.; Korte, L.; Mootz, D. *Z. Naturforsch.* **1981**, *36B*, 1516 and 1660.

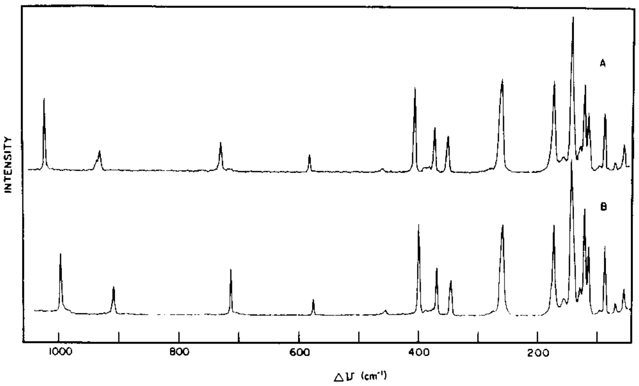


Figure 6. Raman spectra of (A) $S_3N_2Cl_2$ and (B) $S_3{}^{15}N_2Cl_2$ at −196 °C.

Sb–Cl bond lengths of 2.347 (2)–2.380 (3) Å and cis and trans bond angles in the ranges 88.7–91.6 and 177.9–179.4°, respectively. Anion–cation contacts to X(1), X(2), and X(4) are significantly longer than those to the Se and S atoms in $SeS_2N_2Cl_2$ above (Table VII).

^{15}N and ^{77}Se NMR and Vibrational Spectroscopic Data for $SeS_2N_2Cl_2$. The ^{15}N and ^{77}Se NMR spectra were obtained from natural abundance and 99% ^{15}N-enriched $SeS_2N_2Cl_2$ dissolved in 100% sulfuric acid. The ^{15}N NMR spectrum (^{15}N, $I = {}^1/_2$) shows a pair of doublets (at $\delta = -51.7$ and -137.8 ppm) whose coupling constant ($^2J_{^{15}N-^{15}N}$) has almost the same value (5.6 Hz) as that reported for the $S_4N_3{}^+$ species in HNO_3 ($^2J_{^{15}N-^{15}N} = 8.5$ Hz).[42] The ^{77}Se NMR spectra (^{77}Se, $I = {}^1/_2$, and natural abundance = 7.5%)[43] of natural-abundance (^{15}N, 0.37%) and ^{15}N-enriched (99%) $SeS_2N_2Cl_2$, respectively, show a singlet and doublet at $\delta = 326.0$ ppm. These data are consistent with the presence of either the $SeS_2N_2Cl^+$ ion or the $SeS_2N_2Cl_2$ molecule. Because sulfuric acid is a highly ionizing medium, it is reasonable to suppose that the NMR spectra are those for the $SeS_2N_2Cl^+$ cation. The coupling of 117.8 Hz observed in the ^{77}Se NMR spectrum of this species is one of the first examples of a directly bonded $^{77}Se-^{15}N$ coupling. The two-bond coupling between Se and N was not observed.

The vibrational data for $SeS_2N_2Cl_2$ and $SeS_2{}^{15}N_2Cl_2$ are listed in Table VIII along with data for $(S_3N_2Cl^+)Cl^-$. The Raman spectra of $SeS_2N_2Cl_2$, $SeS_2{}^{15}N_2Cl_2$, $S_3N_2Cl_2$, and $S_3{}^{15}N_2Cl_2$ are shown in Figures 5 and 6. Infrared spectra of $S_3N_2Cl_2$ were generally of poor quality, and only the strongest bands are listed. The compound $SeS_2N_2Cl_2$, containing a neutral $SeS_2N_2Cl_2$ molecule having C_s symmetry and a dissymmetric $SeS_2N_2Cl^+$ cation, would be expected to have 27 fundamental vibrations (12 from the cation and 15 from the neutral molecule), while $S_3N_2Cl^+Cl^-$ would be expected to have 12 fundamental vibrations, all of which should be infrared and Raman active. Virtually all the bands in the Raman spectra of $SeS_2N_2Cl_2$ and $S_3N_2Cl^+Cl^-$ are observed to have coincident bands (>250 cm^{-1}) in the infrared spectra. There are no Raman bands between 170 and 259 cm^{-1} for $S_3N_2Cl^+Cl^-$ and only one weak band between 147 and 211 cm^{-1} for $SeS_2N_2Cl_2$, indicating that the lattice vibrations appear to be well separated from the fundamental modes. Above 200 cm^{-1} the 21 and 10 Raman bands observed for $SeS_2N_2Cl_2$ and $S_3N_2Cl_2$, respectively, are in reasonable agreement with the predicted number of bands in view of the fact that there are probably a number of coincidences between the bands of $SeS_2N_2Cl_2$ and those for $SeS_2N_2Cl^+$.

Comparison of some S–S, Se–S, S–Cl, and Se–Cl bond lengths and their corresponding stretching frequencies suggests that the Se–Cl and Se–S stretches in $SeS_2N_2Cl_2$ are likely to occur within the same range of frequencies. The vibrational frequencies of these stretches cannot therefore be assigned with certainty. Indeed, the large number of vibrations that undergo isotope shifts indicates that both $SeS_2N_2Cl_2$ and $S_3N_2Cl_2$ are strongly coupled systems. A comparison of the Raman spectra of $S_3N_2Cl_2$ and $SeS_2N_2Cl_2$ in the region 700–1050 cm^{-1} shows similar bands at ca. 1017, 928, and 728 cm^{-1}. These bands have virtually the same isotopic shift, indicating that the vibrations corresponding to these frequencies must be quite similar. Furthermore, some of the Raman bands in the spectra of $SeS_2N_2Cl_2$ are doublets, most probably arising from the presence of the two species $SeS_2N_2Cl^+$ and $SeS_2N_2Cl_2$. The moderately intense doublet at 539/528 (529/518) cm^{-1} in the Raman spectrum of $SeS_2N_2Cl_2$ ($SeS_2{}^{15}N_2Cl_2$) has no apparent counterpart in the $S_3N_2Cl_2$ spectrum and may arise from a vibration having a pronounced Se–N stretching component.

Supplementary Material Available: Table SI (a population analysis of the disordered sites in the $Se_xS_{3-x}N_2Cl^+$ cations) and Table SII (anisotropic thermal parameters) (4 pages); Table SIII (final structure factor amplitudes) (31 pages). Ordering information is given on any current masthead page.

---

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

[43] Harris, R. K., Mann, B. E., Eds. *NMR and the Periodic Table*; Academic Press: London, 1978.