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Synthesis and Characterization of Selenium–Nitrogen Chlorides: Force-Field Calculations for the $Se_3N_2Cl^+$ Cation

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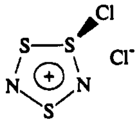
The explosive black solid 3-chloro-1,3,4,2,5-triselenadiazolium chloride, $Se_3N_2Cl_2$, has been prepared in high yield by three different reactions: (a) from $[(Me_3Si)_2N]_2Se$ and a mixture of $SeCl_4$ and Se_2Cl_2 designed to give a Se:Cl ratio of 1:3, (b) from $[(Me_3Si)_2N]_2Se$ and $SeOCl_2$ in a 1:2 molar ratio, and (c) from Me_3SiN_3 and Se_2Cl_2 in a 2:3 molar ratio. The related dimer $(Se_3N_2Cl)_2$ is obtained as an explosive dark brown powder by two routes: (a) from equimolar amounts of Se_4N_4 and Se_2Cl_2 and (b) from $[(Me_3Si)_2]N]_2Se$ and a mixture of $SeCl_4$ and Se_2Cl_2 designed to give a Se:Cl ratio of 2:5. In all reactions the reagents were mixed in dichloromethane at −78 or −30 °C and then allowed to warm up to room temperature. These new selenium–nitrogen chlorides have been identified by complete elemental analyses and by infrared spectroscopy. The fundamental vibrations for the $Se_3N_2Cl^+$ cation were calculated using a general valence force-field approach and were used to assign the infrared spectrum of the cation. The reaction of $Se_3N_2Cl_2$ with SO_2Cl_2 in dichloromethane at −78 °C produces an unstable selenium–nitrogen chloride, characterized by ^{14}N and ^{77}Se NMR spectroscopy, which decomposes to give a mixture of selenium chlorides and N_2.

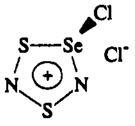
Introduction

The development of inorganic selenium–nitrogen (Se–N) chemistry has been slow[2] compared to the substantial advances that have been made in the area of sulfur–nitrogen (S–N) chemistry in the last 20 years.[3] In part, the preparation of new Se–N compounds has been impeded by the lack of suitable reagents. However, the cage molecule Se_4N_4 has been used as a source of both neutral and ionic Se–N fragments e.g. in the preparation of metal complexes of NSeCl[4] and of the anions Se_3N^- and $Se_2N_2{}^{2-}$.[5] The binary cation $Se_3N_2{}^{2+}$ has been prepared by the oxidation of Se_4N_4 with AsF_5.[6] Very recently the acyclic Se–N–Cl cations $N(SeCl_2)_2{}^+$ and $N(SeCl)_2{}^+$ have been obtained from $(Me_3Si)_3N$ and $SeCl_3{}^+$ or $SeCl_4$, respectively.[7,8]

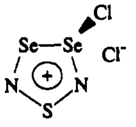
In S–N chemistry, the chlorides $S_3N_2Cl_2$, **1a**, and, especially, $(NSCl)_3$ are important starting materials.[3] Furthermore, the preparation and structural characterization of the five-membered, mixed chalcogen–nitrogen chlorides $SeS_2N_2Cl_2$, **1b**,[9] and $Se_2SN_2Cl_2$, **1c**,[10] have been reported recently. The silylated sulfur diimide $Me_3SiNSNSiMe_3$ provides a rich source of acyclic and cyclic S–N derivatives,[3] but the selenium analogue $Me_3SiNSeNSiMe_3$ is thermally unstable[11] and has found limited applications.[12] By contrast, the selenium(II) reagent $(Me_3Si)_2NSeN(SiMe_3)_2$, **3**, is stable and readily prepared,[10,13] and this reagent can be used as a source of the NSeN fragment. For example, the reaction of **3** with $SeCl_4$ provides an easy route to Se_4N_4.[10,14] Since both Se_2Cl_2 [formally selenium(I)] and $SeCl_4$ are readily available, it is possible to generate selenium in any formal oxidation state between +1 and +4 by using the appropriate stoichiometric mixtures of Se_2Cl_2 and $SeCl_4$.[15] In this paper we describe the application of this strategy to the preparation of $Se_3N_2Cl_2$, **1d**, and $(Se_3N_2Cl)_2$, **2d**, from **3** as well as alternative routes to these Se–N chlorides.[16] Force-field calculations of the fundamental vibrations for the $Se_3N_2Cl^+$ cation have been carried out for comparison with the experimental infrared spectra.[17] Attempts to prepare $(NSeCl)_3$ by the chlorination of **1d** are also reported.



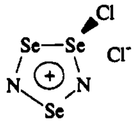
1a



1b



1c



1d

Experimental Section

Reagents and General Procedures. All solvents were dried and freshly distilled under a nitrogen atmosphere before use: dichloromethane (P_4O_{10}), hexane (P_4O_{10}), and diethyl ether (Na/benzophenone). All

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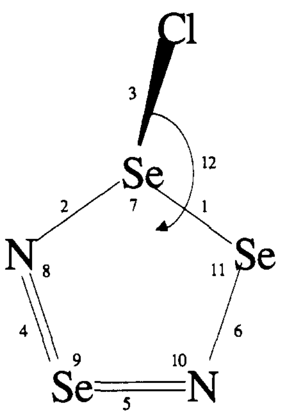

Figure 1. Numbering scheme for bonds and bond angles in $Se_3N_2Cl^+$.

reactions and the manipulations of air- and moisture-sensitive reagents were carried out under an atmosphere of nitrogen (99.99% purity) passed through P_4O_{10}. The commercially available reagents Se_2Cl_2, $(Me_3Si)_2NH$, and Bu^{n}Li (1.6 M solution in hexane) (all from Aldrich), Me_3SiN_3 (Petrarch Systems), $SeOCl_2$ (Strem), and SO_2Cl_2 (Eastman) were used without further purification.

Literature procedures were used for the preparation of $SeCl_4$[18] and Se_4N_4.[19] The compound Se_4N_4 was also prepared by the reaction of $(Me_3Si)_2NLi$ and a mixture of Se_2Cl_2 and $SeCl_4$ using a recently described procedure.[14] The reagent $[(Me_3Si)_2N]_2Se$ [$\delta(^1H)$ (in $CDCl_3$) 0.15, $\delta(^{77}Se)$ (in CH_2Cl_2) 1128.9 ppm [$\delta(^{14}N) = -330$ ppm]; cf. $\delta(^1H)$ 0.27,[13] 0.33[10] and $\delta(^{77}Se)$ 1130 ppm][10] was prepared by the reaction of $(Me_3Si)_2NLi$ with Se_2Cl_2 according to the method of Roesky et al.[13] This product was purified by sublimation, and the residual yellow oil was identified as $[(Me_3Si)_2N]Se_2$ [$\delta(^1H)$ (in $CDCl_3$) 0.13, $\delta(^{77}Se)$ (in CH_2Cl_2) 1028.0 ppm; cf. $\delta(^1H)$ (C_6D_6) 0.28, $\delta(^{77}Se)$ (C_6D_6) 1029 ppm].[10]

Instrumentation. Infrared spectra were recorded as Nujol mulls between KBr or CsI disks on a Mattson 4030 spectrometer. ^1H NMR spectra were obtained by use of a Bruker AC 200 instrument, and chemical shifts are reported relative to neat Me_4Si. The ^{77}Se and ^{14}N NMR spectra were recorded with a Bruker AM-400 instrument operating at 76.31 and 28.92 MHz, respectively. The respective spectral widths were 100.00 and 29.41 kHz, and the resolutions were 6.1 and 3.6 Hz/data point. The ^{77}Se accumulations contained 20 000–30 000 transients, and those for nitrogen, ca. 200 000 transients. All ^{77}Se NMR spectra were referenced externally to a saturated solution of SeO_2 at room temperature. The chemical shifts are reported relative to neat Me_2Se at room temperature [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$]. The ^{14}N NMR spectra are reported relative to neat CH_3NO_2. Elemental analyses for Se (as red selenium), N, and Cl (as AgCl) were obtained by using standard procedures[20] on freshly prepared samples that were mixed with a known amount of dry Nujol in order to minimize the risk of explosions.

Force-Field Calculations. The fundamental vibrations of $Se_3N_2Cl^+$ were calculated using a general valence force-field approach.[21] Initially a simple force field was chosen with 10 diagonal force constants and no interaction force constants. At a later stage of the force constant refinement, however, it became evident that there is interaction between the stretching modes involving bonds of the three-coordinated selenium (i.e. Se–Se, Se–N, and Se–Cl bonds) and the bending mode (Se–Se–Cl). Therefore two interaction force constants were introduced in the *F*-matrix. The molecular geometry of $Se_3N_2Cl^+$ was estimated by use of a semi-empirical PM3 geometry optimization with the program SPARTAN.[22] The geometry thus obtained for **1d** is consistent with that observed for $Se_3N_2Cl^+$ in the $GaCl_4^-$ salt[17] and with those of **1b** and **1c**.[9,10] The numbering scheme of the internal coordinates of $Se_3N_2Cl^+$ is shown in Figure 1.

Table I. Infrared Spectral Data (cm^{-1}) for $Se_3N_2Cl_2$, **1d**, and $(Se_3N_2Cl)_2$, **2d**[a]

$Se_3N_2Cl_2$[b,c]				$(Se_3N_2Cl)_2$[b,c]	
eq 1	eq 2	eq 3	ref 25[d]	eq 4	eq 5
				876 s, sh	
829 s	829 s	829 s	828 s	829 s	829 s, sh
795 w	795 w	791 w	792 w	779 s sh	779 s, sh
	667 w	658 w		652 m	663 m
				639 m	639 w
584 s	584 s	584 s	584 m		
571 s	571 s	571 s	571 s	575 s	575 s
555 vs	556 vs	556 vs	554 s	556 s	556 s
					515 w
				469 w	
417 w	413 w	424 w		419 s	424 s
376 w			352 sh		
324 w	324 w		325 m	340 w	345 w
282 vs	282 vs	282 vs	281 s	290 s	295 s
245 s	245 s	249 s	244 s	245 m	245 m
			169 s		
			126 s		
			105 vw		

[a] As Nujol mulls. In view of the explosive nature of **1d** and **2d**, it is recommended that appropriate precautions be taken in the preparation of mulls. The use of a metal spatula should be avoided. [b] The preparative methods for the different samples of **1d** and **2d** are represented by the equations in the text. [c] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [d] Reaction of trimethylsilyl azide with selenium monochloride in a 4:2 molar ratio in CH_2Cl_2.

The initial values of the force constants were estimated on the basis of those in the $Se_2SN_2^{2+}$ and $Se_3N_2^{2+}$ cations.[23] By adjustment of the observed nine IR bands to the calculated ones, the diagonal force constants were refined by maintaining the existing interaction force constants. Subsequently, the diagonal force constants were held constant and the interaction force constants were refined. This cycle was repeated until no further change was observed. The final calculated and observed fundamental vibrations and the calculated potential energy distribution are shown in Table II. The stretching force constants are compared with those in related molecular species in Table III.

Preparation of $Se_3N_2Cl_2$. *Caution! Dry $Se_3N_2Cl_2$ is explosive under the influence of heat or mechanical stress and should be stored and handled under a hydrocarbon solvent. The preparation of $Se_3N_2Cl_2$ should be limited to amounts of <1.0 g.*

Method a. Reaction of $[(Me_3Si)_2N]_2Se$ with Se_2Cl_2 and $SeCl_4$. A solution of $[(Me_3Si)_2N]_2Se$ (0.200 g, 0.50 mmol) in CH_2Cl_2 (5 mL) was added to a mixture of Se_2Cl_2 (0.0345 g, 0.15 mmol) and $SeCl_4$ (0.143 g, 0.65 mmol) in CH_2Cl_2 (20 mL) at –78 °C. The dark red solution was allowed to warm to room temperature (20 h) to give a black precipitate, which was separated via a filter cannula, washed with CH_2Cl_2 (4 × 10 mL), and identified as $Se_3N_2Cl_2$ (0.16 g, 0.48 mmol, 95% yield). Anal. Calcd for $Cl_2N_2Se_3$: Cl, 21.12; N, 8.34; Se, 70.54. Found: Cl, 20.73, N, 9.02; Se, 70.44. The IR data are summarized in Table I. The ^1H NMR spectrum of the colorless filtrate showed only a signal for Me_3SiCl at 0.39 ppm.

Method b. Reaction of $[(Me_3Si)_2N]_2Se$ with $SeOCl_2$. A solution of $[(Me_3Si)_2N]_2Se$ (0.200 g, 0.50 mmol) in CH_2Cl_2 (5 mL) was added to a solution of $SeOCl_2$ (0.166 g, 1.0 mmol) in CH_2Cl_2 (15 mL) at –78 °C. The dark red solution was allowed to warm to room temperature to give a black precipitate, which was separated via a filter cannula, washed with CH_2Cl_2 (4 × 10 mL), and identified as $Se_3N_2Cl_2$ (0.15 g, 0.45 mmol, 89%). Anal. Calcd for $Cl_2N_2Se_3$: Cl, 21.12; N, 8.34; Se, 70.54. Found: Cl, 19.50; N, 8.08; Se, 73.0. The IR data are summarized in Table I. The ^1H NMR spectrum of the colorless filtrate showed signals of approximately equal intensity at 0.39 and 0.02 ppm, identified as Me_3SiCl and $(Me_3Si)_2O$, respectively, by comparison with the chemical shifts obtained for the pure compounds in CH_2Cl_2.

Method c. Reaction of Me_3SiN_3 with Se_2Cl_2. A cold (–30 °C) solution of trimethylsilyl azide (0.140 g, 1.2 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of Se_2Cl_2 (0.410 g, 1.8 mmol) in CH_2Cl_2 (5 mL) at –30 °C. The reaction mixture was allowed to warm slowly to room temperature, with stirring, to give a black precipitate. This product was isolated by decantation, washed with small portions of CH_2Cl_2 until the filtrate was colorless, and identified as $Se_3N_2Cl_2$ (0.282 g, 0.84 mmol, 70% yield) by IR spectroscopy (see Table I). Anal. Calcd for $Cl_2N_2Se_3$:

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Cl, 21.12; N, 8.34; Se, 70.54. Found: Cl, 19.75; N, 6.90; Se, 70.00. The ^{1}H NMR spectrum of the filtrate showed only a signal for Me_3SiCl at 0.41 ppm.

When the same reaction was carried out using the stoichiometry described in the literature[25] but reducing the amounts of reagents by a factor of 4, $Se_3N_2Cl_2$ was obtained in 88% yield. Anal. Found: Cl, 20.09; N, 7.45; Se, 72.68. The ^{1}H NMR spectrum of the filtrate exhibited singles at 0.26 and 0.39 ppm attributable to Me_3SiN_3 and Me_3SiCl, respectively.

Preparation of $(Se_3N_2Cl)_2$. *Caution! Dry $(Se_3N_2Cl)_2$ is explosive under the influence of heat or mechanical stress and should be stored and handled under a hydrocarbon solvent.*

Method a. Reaction of Se_4N_4 with Se_2Cl_2. A solution of Se_2Cl_2 (0.050 g, 0.20 mmol) in CH_2Cl_2 (5 mL) was added to a slurry of Se_4N_4 (0.080 g, 0.20 mmol) in CH_2Cl_2 (10 mL) at −30 °C. The reaction mixture was allowed to warm slowly to room temperature with stirring. After 16 h the dark brown precipitate was separated via a filter cannula, washed with CH_2Cl_2 (4 × 10 mL), and identified as $(Se_3N_2Cl)_2$ (0.090 g, 0.075 mmol, 75%). Anal. Calcd for ClN_2Se_3: Cl, 11.80; N, 9.33; Se, 78.87. Found: Cl, 11.73; N, 10.25; Se, 76.16. The IR data are summarized in Table I.

Method b. Reaction of $[(Me_3Si)_2N]_2Se$ with Se_2Cl_2 and $SeCl_4$. A solution of $[(Me_3Si)_2N]_2Se$ (0.200 g, 0.50 mmol) in CH_2Cl_2 (5 mL) was added to a mixture of Se_2Cl_2 (0.056 g, 0.25 mmol) and $SeCl_4$ (0.110 g, 0.50 mmol) in CH_2Cl_2 (20 mL) at −78 °C. The reaction mixture became dark red immediately and, upon warming to room temperature, produced a dark brown precipitate and a colorless filtrate. The dark brown precipitate was separated by decantation, washed with CH_2Cl_2 (4 × 10 mL), and identified as $(Se_3N_2Cl)_2$ (0.145 g, 0.121 mmol, 97%). Anal. Calcd for ClN_2Se_3: Cl, 11.80; N, 9.33; Se, 78.87. Found: Cl, 12.42; N, 8.50; Se, 77.50. The IR data are summarized in Table I. The ^{1}H NMR spectrum of the filtrate showed only a signal for Me_3SiCl at 0.39 ppm.

Attempted Preparation of $(NSeCl)_3$: Reaction of $Se_3N_2Cl_2$ with SO_2Cl_2. A mixture of $Se_3N_2Cl_2$ (0.080 g, 0.24 mmol) and an excess of SO_2Cl_2 (0.165 g, 1.20 mmol) in CH_2Cl_2 (2 mL) was transferred to an 8-mm o.d. tube at −78 °C that was subsequently sealed under vacuum. When this mixture was allowed to warm up to room temperature, a deep red solution and a white precipitate were formed. In a separate experiment, conducted in an open vessel under nitrogen, the white precipitate was identified as $SeCl_4$ (IR spectrum).[18] The ^{14}N NMR spectrum of the red solution, obtained by placing the 8-mm tube inside a 10-mm o.d. tube containing D_2O, gave only one signal at +242 ppm. The ^{77}Se NMR spectrum of the same solution gave rise to three signals at +1778 (cf. +1762 for $SeCl_2$ in CH_2Cl_2),[26] +1485, and +1285 ppm (cf. 1280 for Se_2Cl_2).[26]

Results and Discussion

Preparation and Characterization of $Se_3N_2Cl_2$. The reaction of $Se[N(SiMe_3)_2]_2$ with a mixture of selenium chlorides designed to give an Se:Cl ratio of 1:3 in CH_2Cl_2 produced 3-chloro-1,3,4,2,5-triselenadiazolium chloride, $Se_3N_2Cl_2$, **1d**, in 95% yield according to eq 1. The ^{1}H NMR spectrum of the filtrate revealed the exclusive presence of chlorotrimethylsilane.

$$3[(Me_3Si)_2N]_2Se + 4SeCl_4 + Se_2Cl_2 \rightarrow 3Se_3N_2Cl_2 + 12Me_3SiCl \quad (1)$$

The product **1d** was obtained as an explosive, black powder, which is insoluble in organic solvents and in liquid SO_2. This compound is both moisture-sensitive and thermally unstable at room temperature.[27] Consequently, it is essential to carry out elemental analyses on freshly prepared samples. In addition, it is necessary to mix these samples with a weighed amount of Nujol in order to minimize the risk of explosions during the analytical procedures. Under these circumstances, it was possible to obtain good analytical data (Cl, N, Se) for **1d** prepared in this manner.

The same compound was also obtained by two other procedures, which, on the basis of analytical data, give slightly less pure products than eq 1. The reaction of $[(Me_3Si)_2N]_2Se$ with selenium oxo dichloride in CH_2Cl_2 proceeded cleanly at room temperature to give $Se_3N_2Cl_2$ in 89% yield. The ^{1}H NMR spectrum of the filtrate revealed only the presence of chlorotrimethylsilane and hexamethyldisiloxane consistent with the stoichiometry shown in eq 2.

$$[(Me_3Si)_2N]_2Se + 2SeOCl_2 \rightarrow Se_3N_2Cl_2 + 2Me_3SiCl + (Me_3Si)_2O + {}^{1}/_{2}O_2 \quad (2)$$

The third method for the preparation of **1d** involves the reaction of selenium monochloride with trimethylsilyl azide. This reaction has been reported to give Se_4N_2, but no analytical data were given.[25] We found, however, that when the reaction was carried out using the stoichiometry described in the literature,[25] the filtrate contained substantial amounts of unreacted trimethylsilyl azide (^{1}H NMR). Consequently, we adjusted the stoichiometry to that illustrated in eq 3 and obtained $Se_3N_2Cl_2$ in 70% yield. Trimethylsilyl azide was completely consumed and chlorotrimethylsilane was the exclusive product in the filtrate as determined by the ^{1}H NMR spectrum.

$$3Se_2Cl_2 + 2Me_3SiN_3 \rightarrow 2Se_3N_2Cl_2 + 2Me_3SiCl + N_2 \quad (3)$$

In fact, the reaction of selenium monochloride with trimethylsilyl azide in dichloromethane was first reported by Passmore and co-workers 10 years ago.[28a] These authors described their product as a blue-black, explosive solid and suggested that the IR spectrum was "not inconsistent with the formation of Se–N compounds, if not $(SeN)_x$."

The insolubility and explosive nature of $Se_3N_2Cl_2$ severely limits its characterization by spectroscopic methods, e.g. NMR and mass spectroscopy. The IR spectra of $Se_3N_2Cl_2$ prepared by different methods are compared in Table I.[28b] The congruence between the IR data for samples prepared by the three different methods represented by eqs 1–3 provides unequivocal evidence that the same product is formed in all three reactions. Furthermore, the similarity between these data and those reported by Dehnicke et al.[25] strongly suggest that their product was also $Se_3N_2Cl_2$ and not Se_4N_2 as claimed. There are only a few reports of IR spectroscopic studies for Se–N rings. From the published IR spectra of Se_4N_4[29] and $Se_3N_2^{2+}$,[30] it can be inferred that ν(Se=N) and ν(Se–N) will be observed in the regions ca. 800–900 and ca. 500–600 cm^{-1}, respectively. Our force-field calculations (see Table II) indicate that the strong band at 829 cm^{-1} and the weak band at 795 cm^{-1} are both attributable to the stretching modes of the N=Se=N fragment, while the two bands at 584 and 571 cm^{-1} are mainly due to ν(Se–N) modes, though minor contributions from the bending modes can be seen in the potential energy distribution shown in Table II. The main contribution to the weak band at 324 cm^{-1} is ascribed to ν(Se–Se), and that of the strong band at 282 cm^{-1}, to ν(Se–Cl).[31] The structure of **1d** is represented as ionic, $Se_3N_2Cl^+Cl^-$, by analogy with those of **1a**,[32] **1d**,[9] and **1c**.[10] However, we note that covalent forms of **1b**,**c**, in which both chlorines are attached to the same

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(27) Cl analyses for two different 1-week-old samples gave low values, 13.4 and 15.8%, indicating that the compound decomposes slowly at room temperature with loss of chlorine. Samples of **1d** should be stored at −20 °C in order to minimize this decomposition.

(28) (a) Kennett, F. A.; MacLean, G. K.; Passmore, J.; Rao, M. N. S. *J. Chem. Soc., Dalton Trans.* **1982**, 851. (b) A blue-black product obtained from the reaction of Me_3SiN_3 with $SeBr_4$ in acetonitrile was reported to exhibit IR bands at 815 s, 790 w, 572 s, and 545 m cm^{-1} and, therefore, may contain $Se_3N_2Cl_2$.

(29) Adel, J.; Ergezinger, C.; Figge, R.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43b*, 639.

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

(31) A band at 340 cm^{-1} has been attributed, without explanation, to ν_{Se-Cl} for **1c** in the text of ref 10, but the low-frequency bands are reported to occur at 358, 309, and 297 cm^{-1} in the experimental section.

(32) Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Inorg. Chem.* **1968**, *30*, 2851.

Table II. Calculated and Observed Fundamental Vibrations (cm^{-1}) of $Se_3N_2Cl^+$ and the Calculated Potential Energy Distribution (%) along the Internal Coordinates[a]

		stretching modes						bending modes							
calc	obs	1, ν(Se–Se)	2, ν(Se–N)	3, ν(Se–Cl)	4, ν(Se═N)	5, ν(Se═N)	6, ν(Se–N)	7, δ(N–Se–Se)	8, δ(Se═N–Se)	9, δ(N═Se═N)	10, δ(Se–N═Se)	11, δ(Se–Se–N)	12, δ(Se–Se–Cl)	tors[b]	wag[c]
829	829				40	45									
795	795		10		45	35	10								
584	584		10				40				20				
571	571		45				20		15						
555	555													90	
417	417												30	25	20
324	324	40											25	15	
282	282			65											
245	245	40		20									25		
209			10				10		20	20	15				
183								15	10		20	15			10
109														15	45

[a] For the definition of internal coordinates, see Figure 1. The potential energy contributions have been rounded to the nearest 5%. Minor contributions <10% are not shown. [b] Torsional. [c] Wagging.

Table III. Stretching Force Constants of $Se_3N_2Cl^+$

force cons, N m^{-1}	$Se_3N_2Cl^{+\,a}$	$Se_3N_2^{2+\,b}$	$\overline{\mathrm{SeNSNSe}}^{2+\,b}$	$Se_2Cl_2{}^c$
f_{SeSe}	190	222	200	198
f_{Se-N}	220, 231	292		
$f_{Se=N}$	391	390	404	
f_{Se-Cl}	117			192

[a] This work. [b] Reference 23. [c] Reference 24.

selenium atom, have been structurally characterized.[9,10] The highly insoluble character of **1d** is consistent with an ionic structure and may also indicate significant intermolecular interactions as found for Se_4N_4.[33]

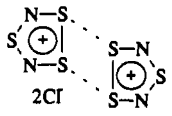
Since the $Se_3N_2{}^{2+}$ cation has been characterized recently,[30] we attempted to convert **1d** to $[Se_3N_2][AsF_6]_2$ by the reaction with silver hexafluoroarsenate in CH_2Cl_2 or liquid SO_2. However, no significant reaction was observed over a period of several days probably due to the insolubility of **1d**. Attempts to convert **1d** to more soluble salts by treatment with chloride ion acceptors such as $AlCl_3$ or $SnCl_4$ were also unsuccessful probably for the same reason.[17]

The reaction of $S_3N_2Cl_2$, **1a**, with anhydrous formic acid is known to produce the soluble compound S_3N_2O in good yields.[34] However, no reaction was observed between **1d** and formic acid even at reflux and Se_3N_2O could not be obtained by this route.

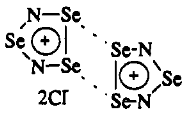
Preparation and Characterization of $(Se_3N_2Cl)_2$. The compound $(S_3N_2Cl)_2$, **2a**, is one of the oldest known S–N compounds.[35] The dimeric structure of this dark green (almost black), highly insoluble solid has been established only recently.[36] It can be prepared in essentially quantitative yields by the reaction of S_4N_4 with S_2Cl_2, either in cold nitromethane or without a solvent.[35] Consequently we started our attempts to prepare $(Se_3N_2Cl)_2$ by investigating the corresponding reaction of Se_4N_4 and $SeCl_2$ in dichloromethane. This reaction proceeded in a straightforward manner to give $(Se_3N_2Cl)_2$ in 75% yield (eq 4).

$$Se_4N_4 + Se_2Cl_2 \rightarrow (Se_3N_2Cl)_2 \qquad (4)$$

The product $(Se_3N_2Cl)_2$ is an explosive, insoluble dark brown powder, which is moisture-sensitive and decomposes slowly at room temperature. Although it is not as prone to explosions as $Se_3N_2Cl_2$, the same precautions were observed in handling this compound. Complete elemental analyses were in good agreement with the empirical formula Se_3N_2Cl, and a dimeric structure, **2d**, is suggested by analogy with that of **2a**.[36]



2a



2d

Similar structures have been proposed for the mixed S–Se analogues $(SeS_2N_2Cl)_2$, **2b**,[10] and $(Se_2SN_2Cl)_2$, **2c**,[15] but these have not been confirmed by X-ray crystallography. The dimer **2d** may also be obtained in essentially quantitative yield by adaptation of the procedure used by Wolmershäuser et al. for the preparation of **2c**.[15] The ^{1}H NMR spectrum of the filtrate confirmed the complete conversion of $[(Me_3Si)_2N]_2Se$ into chlorotrimethylsilane according to eq 5.

$$2[(Me_3Si)_2N]_2Se + Se_2Cl_2 + 2SeCl_4 \rightarrow (Se_3N_2Cl)_2 + 8Me_3SiCl \qquad (5)$$

The IR spectroscopic data for $(Se_3N_2Cl)_2$ prepared by eqs 4 and 5 are compared in Table I. Although there are some discrepancies for the weak bands, the good agreement between the frequencies of the strong IR vibrations, together with the complete analytical data, leave no doubt that $(Se_3N_2Cl)_2$ is produced in both reactions. Not surprisingly, the IR spectrum of **2d** closely resembles that of **1d**. Thus, the bands at 829 and 779 cm^{-1} for **2d** are assigned to ν_{as}(NSeN) and ν_s(NSeN), respectively. The strong bands at 556 and 575 cm^{-1} are attributed to Se–N vibrations.

Reaction of $Se_3N_2Cl_2$ with Sulfuryl Chloride. The chlorination of $S_3N_2Cl_2$, **1a**, with either Cl_2 or SO_2Cl_2 produces $(NSCl)_3$,[37] an important reagent in S–N chemistry.[3] It was, therefore, of interest to discover whether the selenium analogue $(NSeCl)_3$ could be prepared in a similar manner. In preliminary experiments it was demonstrated that the reaction of **1d** with sulfuryl chloride in CH_2Cl_2 in molar ratios varying from 1:1 to 1:6 produces a red solution and a white precipitate of selenium tetrachloride. Subsequently, the reaction was carried out in a sealed tube under vacuum using a molar ratio of 1:4 and the soluble products were investigated by ^{14}N and ^{77}Se NMR spectroscopy. The red solution exhibits a ^{14}N NMR resonance at +242 ppm ($\nu_{1/2}$ = 468 Hz) and ^{77}Se NMR resonances at +1778 ($SeCl_2$), +1485, and +1285 ppm (Se_2Cl_2). Thus the red color of the solution may be due to the formation of Se_2Cl_2 rather than the nitrogen-containing species. After 1 week at 23 °C the same sample showed only a very weak ^{14}N signal at +242 ppm and a strong resonance at −70

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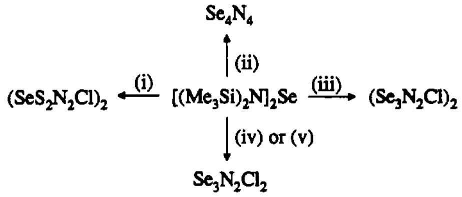
ppm attributable to N_2,[38] presumably formed by the decomposition of the +242 ppm species. In the ^{77}Se NMR spectrum the signal at +1485 ppm was no longer present in the 1-week-old sample, while those attributable to $SeCl_2$ and Se_2Cl_2 had intensified.

The NMR spectroscopic evidence suggests that the chlorination of **1d** produces a thermally unstable Se–N chloride, which decomposes to give a mixture of selenium chlorides and dinitrogen. The most likely candidates are either $ClN{=}SeCl_2$ or Cl_2NSeCl_3. The preparation of the thermally unstable compounds $R_FN{=}SeCl_2$ (R_F = CF_3, C_2F_5) has been reported.[39] These pale yellow derivatives decompose quickly at room temperature to give $R_FN{=}NR_F$, $SeCl_4$, and Se_2Cl_2. By analogy, the decomposition of $ClN{=}SeCl_2$ could give rise to N_2, $SeCl_4$, and Se_2Cl_2.[40] We note that the ^{14}N chemical shift of $(Me_3Si)_2NSeN(SiMe_3)_2$ occurs at ca. −330 ppm[41] so it is unlikely that the ^{14}N resonance at +242 ppm is caused by a singly-bonded Se–N species such as Cl_2NSeCl_3.

Conclusion

The selenium–nitrogen halides $Se_3N_2Cl_2$ and $(Se_3N_2Cl)_2$ have been prepared by several procedures. The purest products are obtained from the reaction of $[(Me_3Si)_2N]_2Se$ with a mixture of $SeCl_4$ and Se_2Cl_2 designed to give the appropriate Se:Cl ratio. The versatility of this reagent for the preparation of simple Se–N compounds is noteworthy (see Scheme I). Force-field calculations indicate that $Se_3N_2Cl_2$ contains the $Se_3N_2Cl^+$ cation. However, preliminary investigations indicate that the explosive nature and insolubility of $Se_3N_2Cl_2$ will impose limitations on its use as a reagent in Se–N chemistry. The chlorination of $Se_3N_2Cl_2$ produces a thermally unstable Se–N chloride, possibly $ClN{=}SeCl_2$, rather than $(NSeCl)_3$.

Scheme I. Use of $[(Me_3Si)_2N]_2Se$ as a Reagent for the Preparation of Se–N Compounds[a]



[a] (i) SCl_2;[10] (ii) $SeCl_4$;[10,14] (iii) $^1/_2Se_2Cl_2 + SeCl_4$; (iv) $^1/_3Se_2Cl_2 + {}^4/_3SeCl_4$; (v) $SeOCl_2$.

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