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Syntheses of THF Solutions of SeX_2 (X = Cl, Br) and a New Route to Selenium Sulfides Se_nS_{8-n} (*n* = 1−5): X-ray Crystal Structures of $SeCl_2(tht)_2$ and $SeCl_2$·tmtu

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A simple and efficient synthesis of solutions of pure $SeCl_2$ in THF or dioxane (ca. 0.4 M) at 23 °C was achieved by treatment of elemental selenium with an equimolar amount of SO_2Cl_2. $SeCl_2$ was characterized by ^{77}Se NMR and Raman spectra. $SeCl_2$ forms 1:1 or 1:2 adducts with tetramethylthiourea (tmtu) or tetrahydrothiophene (tht), respectively. The crystal structure of $SeCl_2$·tmtu (**1**) reveals a T-shaped geometry [d(Se−Cl) = 2.443(4) Å] with weak intramolecular Se···Cl interactions [d(Se−Cl) = 3.276(4) Å]. Crystals of **1** are triclinic, space group $P\bar{1}$, with $a = 8.473(3)$ Å, $b = 9.236(3)$ Å, $c = 7.709(4)$ Å, $\alpha = 109.90(3)°$, $\beta = 92.26(4)°$, $\gamma = 107.89(3)°$, $V = 532.9(4)$ Å^3, and $Z = 2$. The complex $SeCl_2(tht)_2$ (**2**) adopts a square planar geometry with d(Se−Cl) = 2.4149(8) Å. Crystals of **2** are monoclinic, space group $C2/c$, with $a = 15.6784(8)$ Å, $b = 9.1678(4)$ Å, $c = 9.1246(4)$ Å, $\beta = 110.892(2)°$, $V = 1225.3(1)$ Å,^{3} and $Z = 4$. The reaction of Ph_3PS with $SeCl_2$ gives Ph_3PCl_2 and a complex mixture of selenium sulfides Se_nS_{8-n} ($n = 1-5$), which were identified by ^{77}Se NMR. Halogen exchange between $SeCl_2$ and Me_3SiBr in THF yields thermally unstable $SeBr_2$ (ca. 0.4 M) characterized by ^{77}Se NMR and Raman spectra.

Introduction

Although selenium dihalides, SeX_2 (X = Cl, Br, I), are potentially important reagents for the development of selenium chemistry, the preparation of *pure* compounds has been elusive. In a recent communication Bryce and Chesney described the use of $PhSO_2SeCl$ as a "synthetic equivalent of the inaccessible $SeCl_2$".[1] The combination $SeCl_4/SbPh_3$ has been employed successfully to generate "$SeCl_2$" in situ for the synthesis of Se−N heterocycles,[2] but the separation of Ph_3SbCl_2 from the desired product can be problematic. The dissociation of $SeCl_4$ in the gas phase produces $SeCl_2$, which has been characterized by Raman spectroscopy,[3] a technique that has also been used to investigate the formation of SeX_2 (X = Cl, Br) from elemental selenium and SeX_4 in acetonitrile in the appropriate stoichiometric ratio.[4] ^{77}Se NMR spectroscopy is the best method for the quantitative analysis of mixtures of selenium halides.[5,6] Lamoureux and Milne have used this technique to investigate the composition of "SeX_2" solutions in various solvents.[5b] Such solutions contain substantial amounts (11−37%) of Se_2X_2, in addition to SeX_2.[5d] Thus the facile synthesis of pure selenium(II) halides would be a useful contribution to selenium chemistry.

We now disclose that *pure* $SeCl_2$ may be prepared from elemental selenium and SO_2Cl_2 in THF. The stability of $SeCl_2$ in various solvents has been investigated by ^{77}Se NMR. The Raman spectrum of $SeCl_2$ in THF and the X-ray structures of the adducts $SeCl_2(tht)_2$ (tht = tetrahydrothiophene) and $SeCl_2$·tmtu (tmtu = tetramethylthiourea) have been determined. Reactions of $SeCl_2$ with Ph_3PE (E = S, Se) and a new synthesis of $SeBr_2$ are also described.

Experimental Section

General Procedures. Solvents were dried and distilled twice under an argon atmosphere prior to use: tetrahydrofuran and dioxane (Na/benzophenone); acetonitrile (CaH_2); methylene chloride (P_4O_{10} and CaH_2). All reactions and the manipulations of air- and moisture-sensitive reagents were carried out under an argon atmosphere passed through P_4O_{10}. Selenium powder, SO_2Cl_2, trimethylsilyl bromide, 1,1,3,3-tetramethyl-2-thiourea, and tetrahydrothiophene (all from Aldrich) were used without further purification. Triphenylphosphine sulfide[7] and triphenylphosphine selenide[8] were prepared by literature procedures.

Instrumentation. The ^1H NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200.134 MHz. The spectral width was 1400 Hz, and pulse width, 3.0 μs. The ^{13}C, ^{14}N, and ^{77}Se NMR spectra were recorded on a Bruker AM 400 spectrometer operating at 100.614, 28.915, and 76.312 MHz, respectively. The spectral widths were 23.81, 29.41, and 100.00 kHz, yielding resolutions of 1.45, 3.59, and 6.10 Hz/data point, respectively. The ^{13}C pulse width was 3.50 μs for ^{14}N 20.0 μs and 9.00 μs for ^{77}Se. The ^{13}C accumulations contained 1 000−20 000 transients, those for ^{14}N, 20 000−200 000, and for selenium ca. 15 000 transients. The ^{14}N NMR chemical shifts are reported relative to neat CH_3NO_2. All ^{77}Se NMR spectra were referenced

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(1) Bryce, M. R.; Chesney, A. *J. Chem. Soc., Chem. Commun.* **1995**, 195.

(2) Belluz, P. D. B.; Cordes, A. W.; Kristof, E. M.; Kristof, P. V.; Liblong, S. W.; Oakley, R. T. *J. Am. Chem. Soc.* **1989**, *111*, 9276.

(3) Ozin, G. A.; Van der Voet, A. *J. Chem. Soc. D* **1970**, 896.

(4) Milne, J. *Polyhedron* **1985**, *4*, 65.

(5) (a) Lamoureux, M.; Milne, J. *Can. J. Chem.* **1989**, *67*, 1936. (b) Lamoureux, M.; Milne, J. *Polyhedron* **1990**, *9*, 589. (c) Milne, J.; Williams, A. J. *Inorg. Chem.* **1992**, *31*, 4534. (d) Se_2Cl_2, 11% (in CH_3CN), 31% (in CH_2Cl_2), 37% (in CCl_4); Se_2Br_2, 19% (in CH_3CN).

(6) Steudel, R.; Plinke, B.; Jensen, D.; Baumgart, F. *Polyhedron* **1991**, *10*, 1037.

(7) Bartlett, P. D.; Cox, E. F.; Davis, R. E. *J. Am. Chem. Soc.* **1961**, *83*, 103.

(8) Hartmann, H.; Meixner, A. *Naturwissenschaften* **1963**, *50*, 403.

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externally to a saturated solution of SeO_2 at room temperature. The chemical shifts are reported relative to neat Me_2Se at room temperature [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$]. D_2O was used as an external ^2H lock. The ^{31}P NMR spectra were recorded on a Varian XL 200 spectrometer operating at 80.987 MHz. The spectral width was 13 000 Hz and pulse width 10 μs. Relaxation time used for ^{31}P was 0.4 s. The ^{31}P accumulations contained ca. 3 000 transients. The ^{31}P spectra are reported relative to 85% H_3PO_4 in D_2O.

The Raman spectra were recorded for THF solutions by using a Bruker IFS-66 spectrometer equipped with a FRA-16 Raman unit and a Nd:YAG laser.

Preparation of $SeCl_2$. Neat SO_2Cl_2 (0.270 g, 2.0 mmol) was added by syringe to selenium powder (0.158 g, 2.0 mmol) in a 25 mL round-bottomed flask at 23 °C. The mixture was stirred for 10 min, and 5 mL of THF was added. The solution was stirred for 1 h to give a clear brownish red solution of $SeCl_2$ identified by ^{77}Se NMR and Raman spectra (see Results and Discussion). Removal of the solvent gives $SeCl_2$ as a thermally unstable red oil.

Preparation of $SeBr_2$. Liquid Me_3SiBr (0.61 g, 4.0 mmol) was added by syringe to a freshly prepared solution of $SeCl_2$ (0.30 g, 2.0 mmol) in THF (5 mL) at 23 °C. The mixture was stirred for 15 min to give a dark red-brown solution. Removal of volatiles under vacuum produced $SeBr_2$ as a red-brown solid, which was characterized by ^{77}Se NMR and Raman spectra (see Results and Discussion).

Preparation of $SeCl_2 \cdot$tmtu. A solution of $SeCl_2$ (0.30 g, 2.0 mmol) in THF was added to a solution of tetramethylthiourea (0.264 g, 2.0 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred for 5 min, to give a clear orange solution. The solution was evaporated to half of the original volume and cooled to −20 °C to give a yellow-orange microcrystalline precipitate. The precipitate was separated by filtration and identified as $SeCl_2 \cdot$tmtu (0.52 g, 1.84 mmol, 92%). NMR (δ, ppm) (CD_2Cl_2): ^1H 3.36 (s, CH_3) (cf. lit. δ 3.36 in CH_2Cl_2);[9] ^{13}C 45.05 (s, CH_3); ^{14}N −266; ^{77}Se 1042.

Preparation of $SeCl_2(tht)_2$. A solution of $SeCl_2$ (0.75 g, 5.0 mmol) in THF (10 mL) was added by syringe to tetrahydrothiophene (0.88 g; 10 mmol) at 0 °C. A yellow precipitate was formed immediately, and the mixture was stirred for 15 min. The yellow microcrystalline product was separated by decantation, washed with cold (0 °C) THF, and identified as $SeCl_2(tht)_2$ (1.01 g; 4.25 mmol, 85%). Anal. Calcd for $C_4H_4Cl_2S_2Se$: C, 29.45; H, 4.94. Found: C, 28.76; H, 4.63. NMR (δ, ppm) (CS_2): ^{13}C (0 °C) 33.51 and 31.77; ^{13}C (−10 °C) 34.48 and 31.74; ^{77}Se (21 °C) 1275; ^{77}Se (0 °C) 1299. Crystals of $SeCl_2(tht)_2$ suitable for X-ray crystallography were grown from a CS_2 solution at −20 °C.

Preparation of Se_nS_{8-n} ($n = 1-5$) from Ph_3PS and $SeCl_2$. A solution of $SeCl_2$ (0.30 g, 2.0 mmol) in THF (5 mL) was added to a solution of Ph_3PS (0.59 g, 2.0 mmol) in dichloromethane (10 mL) at 23 °C. After 2 min an orange precipitate was formed. The mixture was stirred for a further 10 min. An orange powder (0.17 g) was separated by filtration, dissolved in CS_2, and identified as a mixture of eight-membered selenium sulfide rings by ^{77}Se NMR (see Results and Discussion). Removal of the solvent produced colorless crystals. The $^{31}P\{^1H\}$ NMR spectrum of this product in CH_2Cl_2 showed major resonance at δ 65.0 ppm for Ph_3PCl_2 (lit. δ 65.5 in $CDCl_3$)[10] and a minor resonance at δ 29.1 ppm corresponding to Ph_3PO (lit. δ 29.3 in CH_2Cl_2).[11]

Reaction of Ph_3PSe and $SeCl_2$. The treatment of Ph_3PSe (0.34 g, 1.0 mmol) in THF (10 mL) with $SeCl_2$ (0.15 g, 1.0 mmol) afforded a dark precipitate of Se_8 (0.153 g, 97%): $\delta(^{77}Se)$ (in CS_2) 614.5 ppm (cf. lit. $\delta(^{77}Se)$ 615 in CS_2).[12] Removal of the solvent from the filtrate gave colorless crystals consisting of Ph_3PCl_2 as the major product with minor amounts of Ph_3PO. $^{31}P\{^1H\}$ NMR (in $CDCl_2$): δ 65.2 and 29.1 ppm.

Table 1. Crystallographic Data for $SeCl_2 \cdot$tmtu (**1**) and $SeCl_2(tht)_2$ (**2**)

formula	$C_5H_{12}Cl_2N_2SSe$	$C_8H_{16}Cl_2S_2Se$
fw	282.09	326.19
cryst system	triclinic	monoclinic
space group	$P\bar{1}$(No. 2)	$C2/c$
a, Å	8.473(3)	15.6784(8)
b, Å	9.236(3)	9.1678(4)
c, Å	7.709(4)	9.1246(4)
α, deg	109.90(3)	90
β, deg	92.26(4)	110.892(2)
γ, deg	107.89(3)	90
V, Å^3	532.9(4)	1225.3(1)
Z	2	
T, K	170(2)	173(2)
ρ_{calc}, g cm^{-3}	1.758	1.768
μ(Mo Kα), cm^{-1}	41.67	37.97
radiation, λ, Å	0.710 69	0.710 73
R,[a] R_w	0.052, 0.048[a]	0.038, 0.092[b]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$. [b] $_wR = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o{}^2)^2]\}^{1/2}$.

X-ray Analyses. Crystallographic data for **1** and **2** are summarized in Table 1. An orange needle (0.38 × 0.12 × 0.10 mm) of $SeCl_2 \cdot$tmtu obtained by recrystallization from CH_2Cl_2 was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer. The cell constants and an orientation matrix for data collection were determined from the setting angles of 13 reflections in the range of $16.51° < 2\theta < 25.10°$. Scans of $(1.57 + 0.34 \tan \theta)°$ were made at a speed of 4.0° min^{-1} to a maximum 2θ value of 55.1°. The intensities of 2449 reflections were measured, of which 1077 had $I > 3.00\ \sigma(I)$. The data for **1** and **2** were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure of **1** was solved by direct methods[13a] and Fourier techniques.[13b] The non-hydrogen atoms were refined anisotropically. H atoms were constrained to idealized positions (C−H = 0.95 Å). Conventional atomic scattering factors, corrected for anomalous dispersion, were used[14] and allowance was made for anomalous dispersion. All calculations were performed using teXsan.

A yellow needle of $SeCl_2(tht)_2$ (0.40 × 0.05 × 0.05 mm) was mounted on a glass fiber. Diffraction data were collected on a Nonius kappa CCD diffractometer by recording 360 frames via φ-rotation ($\Delta\varphi = 1°$; two times 20 s per frame). There were 1426 unique reflections ($6.40 < 2\theta < 55.74°$) of which 1242 had $I > 2.00\sigma(I)$. The structure of **2** was solved by direct methods using SHELXS-97[15] and refined using SHELXL-97.[15] After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions (C−H = 0.95 Å). In the final refinement the hydrogen atoms were riding with the carbon atom to which they were bonded. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.5 times that of the corresponding carbon atoms. The scattering factors for the neutral atoms were those incorporated with the programs.

Force-Field Calculations. Fundamental vibrations were calculated for $SeCl_2$ and $SeBr_2$ using a general valence force-field approach.[16] The F-matrix of both SeX_2 species contained two diagonal force

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(9) Wynne, K. J.; Pearson, P. S.; Newton, M. G.; Golen, J. *Inorg. Chem.* **1972**, *11*, 1192.

(10) Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G.; Sheffield, J. M. *Chem. Commun.* **1996**, 2521.

(11) Burford, N.; Royan, B. W.; Spence, R. E.v. H. *J. Chem. Soc., Dalton Trans.* **1990**, 2111.

(12) (a) Laitinen, R. S.; Pakkanen, T. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1381. (b) Laitinen, R. S.; Pakkanen, T. A. *Inorg. Chem.* **1987**, *26*, 2598. (c) Pekonen, P.; Taavitsainen, J.; Laitinen, R. S. *Acta Chem. Scand.* **1998**, *52*, 1188.

(13) (a) SIR92: Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343. (b) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program system. Technical Report of the Crystallography Laboratory*; University of Nijmegen: Nijmegen, The Netherlands, 1994.

(14) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(15) Sheldrick, G. M. SHELXS-97. Program for Crystal Structure Determination, University of Göttingen, 1997.

(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.

Table 2. $\delta(^{77}Se)$ for $SeCl_2$ in Various Solvents

$\delta(^{77}Se)$	solvent	ref
1828	THF	*a*
1814	dioxane	*a*
1784	MeCN	*a*
1773	MeCN	*b*
1762	CH_2Cl_2	*b*
1748	CCl_4	*b*

[a] This work; chemical shifts are quoted relative to Me_2Se (0 ppm). [b] Data taken from ref 5b; chemical shifts were reported relative to H_2SeO_3 but are quoted here with reference to Me_2Se [$\delta(Me_2Se) = \delta(H_2SeO_3) + 1302.6$].

constants and one off-diagonal interaction force constant (adjacent SeX/SeX bond−bond interaction). The stretch−bend interaction was assumed to be negligible. The molecular geometry of $SeCl_2$ was taken from the electron diffraction determination by Fernholt et al.[17] The molecular geometry of $SeBr_2$ was estimated by scaling the bond length taking the relative magnitudes of the covalent radii of chlorine and bromine into account. The BrSeBr bond angle in $SeBr_2$ was assumed to be identical to the ClSeCl bond angle in $SeCl_2$.

The initial values of the force constants were taken from the force-field calculations of Milne for $SeCl_2$ and $SeBr_2$.[4] The force constants in both cases were refined simultaneously by adjusting the observed three Raman bands to the calculated values until no further change was observed.

Results and Discussion

Preparation and Spectroscopic Characterization of $SeCl_2$ and $SeBr_2$. Selenium dichloride can be prepared conveniently by the treatment of elemental selenium with SO_2Cl_2 in THF, dioxane, or acetonitrile (eq 1). In CH_2Cl_2, however, $SeCl_2$ is not formed in significant amounts.

$$Se + SO_2Cl_2 \rightarrow SeCl_2 + SO_2(g) \qquad (1)$$

The reaction yields a clear brownish red solution, which was shown to contain $SeCl_2$ by ^{77}Se NMR spectroscopy (see Table 2). In THF at 25 °C a singlet is observed at δ 1828 and the resonance for Se_2Cl_2 at δ 1325 is not observed until 24 h has elapsed. After 1 week the solution contains Se_2Cl_2 (60%) and $SeCl_4$ (40%). The formation of Se_2Cl_2 is apparent after 6 h in both dioxane (96% $SeCl_2$ and 4% Se_2Cl_2) and MeCN (91% $SeCl_2$ and 9% Se_2Cl_2) solutions. In dioxane the resonance for $SeCl_4$ (δ 1505), the other disproportionation product (eq 2), is observed after 24 h. Complete removal of solvent from the freshly prepared solutions in THF produces $SeCl_2$ as a deep red oil, which disproportionates rapidly (eq 2).

$$3SeX_2 \rightleftarrows Se_2X_2 + SeX_4 \qquad (2)$$

$$X = Cl, Br$$

The Raman spectrum of $SeCl_2$ in THF is shown in Figure 1. Identical spectra were obtained at −100 and 23 °C. Three bands are observed at 372, 346, and 168 cm^{-1} corresponding to the symmetric and asymmetric stretching vibrations (ν_1 and ν_3) and the deformation band (ν_2), respectively. In the gas phase $SeCl_2$ exhibits these bands at 415, 377, and 153 cm^{-1},[3] and in MeCN solution the corresponding values are 412, 381, and 165 cm^{-1}.[18] The lower frequencies for the stretching vibrations in THF may reflect coordination of the donor solvent molecules to $SeCl_2$.

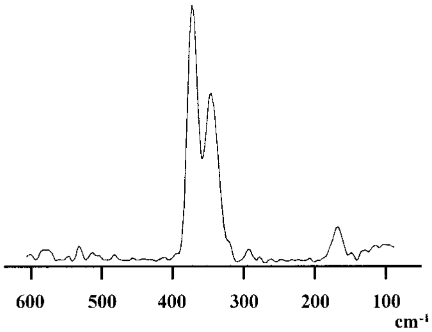

Figure 1. Raman spectrum of $SeCl_2$ in THF at 23 °C (128 scans, resolution ±2 cm^{-1}).

Table 3. Calculated and Observed Fundamental Vibrations (cm^{-1}) of SeX_2 (X = Cl, Br) and the Main Contributions in the Calculated Potential Energy Distribution (PED) along the Internal Coordinates

	obsd	calcd	mode	PED (%)
$SeCl_2$	372	372.9	a_1	ν(SeCl) 96, δ(ClSeCl) 4
	346	346.0	b_2	ν(SeCl) 100
	168	168.0	a_1	δ(ClSeCl) 97, ν(SeCl) 3
$SeBr_2$	261	260.9	a_1	ν(SeBr) 88, δ(BrSeBr) 11
	221	221.1	b_2	ν(SeBr) 100
	110	109.5	a_1	δ(BrSeBr) 91, ν(SeBr) 9

Milne has investigated the formation of $SeBr_2$ from the reaction of elemental selenium with stoichiometric amounts of either $SeBr_4$[4] or bromine[5b] by ^{77}Se NMR and Raman spectroscopy. In this work we found that $SeBr_2$ can be readily obtained in THF solution by halogen exchange between freshly prepared $SeCl_2$ and trimethylsilyl bromide (eq 3).

$$SeCl_2 + 2Me_3SiBr \rightarrow SeBr_2 + 2Me_3SiCl \qquad (3)$$

This reaction yields a dark brownish-red solution containing $SeBr_2$, which was identified by ^{77}Se NMR and Raman spectroscopy. The ^{77}Se NMR resonance for $SeBr_2$ in THF at 25 °C was observed at δ 1584 (cf. $\delta(^{77}Se)$ 1477 in CH_2Cl_2),[5b] but disproportionation to Se_2Br_2 ($\delta(^{77}Se)$ 1217, cf. $\delta(^{77}Se)$ 1174 in CD_2Cl_2)[5b] was already apparent after 1 h. This disproportionation is complete after 12 h.

The Raman spectrum of $SeBr_2$ in THF shows characteristic bands at 261 and 221 cm^{-1} (symmetric (ν_1) and asymmetric (ν_3) stretching vibrations) and at 110 cm^{-1} (deformation (ν_2) band). The literature values for a solution of $SeBr_2$ in MeCN are 290, 266, and 96 cm^{-1}.[4] In this work the Raman spectrum of $SeBr_2$ in THF was obtained for a reaction mixture containing Me_3SiCl (eq 2). The Raman spectrum of Me_3SiCl in THF was also recorded. Evaporation of the solvent produces a dark red-brown solid which disproportionates almost immediately to give Se_2Br_2 and Br_2. It is likely that SeI_2 may also be generated by the halogen exchange reaction (eq 3). However, in view of the relatively low thermal stability of SeI_2[19] (compared to that of $SeBr_2$), this route was not pursued.

Force-field calculations verify the spectroscopic assignments for SeX_2 (X = Cl, Br). The calculated and observed wavenumbers together with the potential energy distributions are given in Table 3. The vibrations at 372 and 261 cm^{-1} are mainly symmetric Se−Cl and Se−Br stretching vibrations, respectively, with a minor contribution by the bending mode in both cases. The vibrations at 346 and 221 cm^{-1} are asymmetric Se−Cl and Se−Br stretching vibrations, respectively, and the Raman lines at 168 and 110 cm^{-1} are mainly bending modes.

The valence force constants of $SeCl_2$ and $SeBr_2$ are presented in Table 4 and compared with those calculated previously.[4]

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(17) Fernholt, L.; Haaland, A.; Seip, R.; Kniep, R.; Korte, L. *Z. Naturforsch.* **1983**, *33b*, 1072.

(18) The band at 381 cm^{-1} is partially obscured by a solvent band at 370 cm^{-1} (see ref 4).

Table 4. Valence Force Constants (N m^{-1}) of SeX$_2$ (X = Cl, Br)

	SeCl$_2$		SeBr$_2$	
	a	*b*	*a*	*b*
f(SeX)	182	225,[c] 225[d]	131	176[c]
f(XSeX)	22	23,[c] 27[d]	20	5[c]
f(SeX/SeX)	14	21,[c] 18[d]	20	14[c]

[a] This work; THF solution. [b] Reference 5. [c] MeCN solution. [d] Vapor phase.

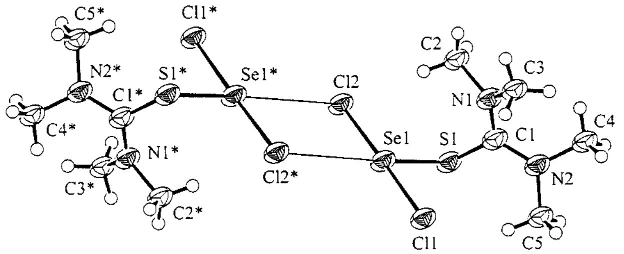

Figure 2. ORTEP drawing (50% probability ellipsoids) and atomic numbering scheme for SeCl$_2\cdot$tmtu.

There is general agreement between the force constants calculated in this work and those by Milne.[4] The somewhat smaller values for the Se−X stretching force constants are a consequence of the appearance of the corresponding vibrations at lower wavenumbers in THF compared to the gaseous species. It can be concluded that both the fundamental vibrations and the force constants of SeCl$_2$ and SeBr$_2$ calculated in this work bear an expected relationship to each other and indicate that the interaction between both molecules with THF is quite similar.

Preparation and X-ray Structures of SeCl$_2$•tmtu (1) and SeCl$_2$(tht)$_2$ (2). The reaction of 1,1,3,3-tetramethylthiourea with SeCl$_2$ in a CH$_2$Cl$_2$/THF solvent mixture (2:1) at 0 °C produced SeCl$_2\cdot$tmtu (**1**) as a yellow-orange microcrystalline solid in ca. 92% yield. The adduct **1** was previously obtained in 50% yield from the reaction of MeSeCl$_3$ (or SeCl$_4$) and tmtu.[9] It was characterized by ^{1}H NMR and IR/Raman spectra.[9] In this work **1** was identified by ^{1}H, ^{13}C, ^{14}N, and ^{77}Se NMR spectroscopy (see Experimental Section) and by an X-ray structure determination. An ORTEP drawing is displayed in Figure 2, and the bond lengths and bond angles are compared with those for SeBr$_2\cdot$tmtu[9] in Table 5. The main structural features of SeX$_2\cdot$tmtu (X = Cl, Br) are similar, and detailed comparisons are not warranted. The adduct **1** consists of T-shaped molecules joined into dimers by weak Se···Cl contacts (3.276 Å; cf. 3.8 Å for sum of van der Waals radii). The almost linear ClSeCl unit (177.2°) has significantly different Se−Cl bond distances (2.475(4) and 2.410(4) Å), the shorter of which is engaged in the intermolecular interactions.

In view of our observations that SeCl$_2$ is stabilized in THF solution or by adduct formation with the sulfur ligand tmtu, we investigated the reaction of SeCl$_2$ with tetrahydrothiophene (tht). In THF at 0 °C this reaction gave rise to the 1:2 adduct SeCl$_2$(tht)$_2$ (**2**) as thermally unstable, yellow microcrystals which are sparingly soluble in CS$_2$. This complex decomposes within 30 min at 23 °C, but it can be stored in the solid state at −20 °C for weeks without decomposition. In CS$_2$ solution, however, decomposition occurs within 48 h even at −20 °C. Complex **2** was identified by ^{13}C and ^{77}Se NMR spectroscopy and by an X-ray structure determination. An ORTEP drawing is illustrated in Figure 3. Bond lengths and bond angles are summarized in Table 6. The complex **2** forms a trans square planar complex with d(Se−Cl) = 2.4149(8) Å and ∠ClSeCl = ∠SSeS = 180.0°. The two tht ligands in this centrosymmetric complex are tilted in opposite directions above and below the SeS$_2$Cl$_2$ plane. Although both cis and trans isomers of TeCl$_2$(tmtu)$_2$ are known,[20] complex **2** represents the first bis-adduct of SeCl$_2$. The Se−Cl bond distances in the adducts SeCl$_2$(tht)$_2$ and SeCl$_2$(tmtu) are 0.26−0.34 Å longer than the value of 2.157(3) Å observed for SeCl$_2$ in the gas phase,[21,22] presumably as a result of three center−four electron bonding in the adducts.

Table 5. Selected Bond Lengths and Bond Angles for SeX$_2\cdot$tmtu (X = Cl,[a] Br[b])

Bond Lengths (Å)

Se(1)−Cl(1)	2.475(4)	Se(1)−Br(1)	2.620(3)
Se(1)−Cl(2)	2.410(4)	Se(1)−Br(2)	2.569(3)
Se(1)−Cl(2)*[c]	3.276(4)	Se(1)−Br(1)	3.34
Se(1)−S(1)	2.216(4)	Se(1)−S(1)	2.212(4)
S(1)−C(1)	1.767(10)	S(1)−C(1)	1.751(15)
N(1)−C(1)	1.318(14)		
N(1)−C(2)	1.459(14)		
N(1)−C(3)	1.448(15)		
N(2)−C(1)	1.347(13)		
N(2)−C(4)	1.461(14)		
N(2)−C(5)	1.461(15)		

Bond Angles (deg)

Cl(1)−Se(1)−Cl(2)	177.17(18)	Br(1)−Se(1)−Br(2)	174.70(10)
Cl(1)−Se(1)−S(1)	89.93(14)	Br(1)−Se(1)−S(1)	91.31(13)
Cl(2)−Se(1)−S(1)	92.90(14)	Br(2)−Se(1)−S(1)	93.71(14)
Se(1)−S(1)−C(1)	101.8(4)	Se(1)−S(1)−C(1)	102.3(5)
C(1)−N(1)−C(2)	122.6(11)		
C(2)−N(1)−C(3)	114.4(11)		
C(1)−N(2)−C(4)	121.7(10)		
C(1)−N(2)−C(5)	124.0(10)		
C(4)−N(2)−C(5)	113.9(9)		
S(1)−C(1)−N(1)	123.2(9)		
S(1)−C(1)−N(2)	115.8(9)		
N(1)−C(1)−N(2)	121.0(11)		

[a] This work. [b] Preliminary results for the structure of SeBr$_2\cdot$tmtu are reported in ref 9. [c] Starred atoms are related by the symmetry operation −*x*, −*y* + 1, −*z*.

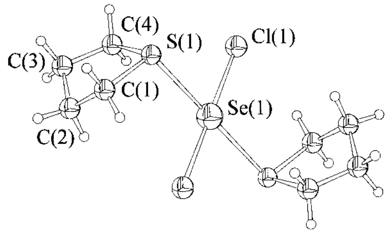

Figure 3. ORTEP drawing (50% probability ellipsoids) and atomic numbering scheme for SeCl$_2$(tht)$_2$.

Table 6. Selected Bond Lengths and Bond Angles for SeCl$_2$(tht)$_2$[a]

Bond Lengths (Å)

Se(1)−Cl(1)	2.4149(8)	C(1)−C(2)	1.520(4)
Se(1)−S(1)	2.5494(8)	C(2)−C(3)	1.524(5)
Se(1)−C(1)	1.820(3)	C(3)−C(4)	1.526(5)
S(1)−C(4)	1.831(3)		

Bond Angles (deg)

Cl(1)−Se(1)−S(1)	82.70(3)	Se(1)−S(1)−C(4)	98.67(12)
Cl(1)−Se(1)−S(1)*	97.30(3)	C(1)−S(1)−C(4)	93.99(15)
Se(1)−S(1)−C(1)	106.84(12)		

[a] Symmetry transformations (starred) used to generate equivalent atoms: −*x*, −*y* + 1, −*z*.

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(19) Gopal, M.; Milne, J. *Inorg. Chem.* **1992**, *31*, 4530.

(20) (a) Foss, O.; Maartmann-Moe, K. *Acta Chem. Scand.* **1986**, *A40*, 675. (b) Chivers, T.; Parvez, M.; Sandblom, N. Unpublished observations.

(21) Fernholt, L.; Haaland, A.; Seip, R.; Kniep, R.; Korte, L. *Z. Naturforsch.* **1983**, *38b*, 1072.

(22) For information on Se−Cl bond distances, see also: Brownridge, S.; Cameron, T. S.; Passmore, J.; Schatte, G.; Way, T. C. *J. Chem. Soc., Dalton Trans.* **1996**, 2553.

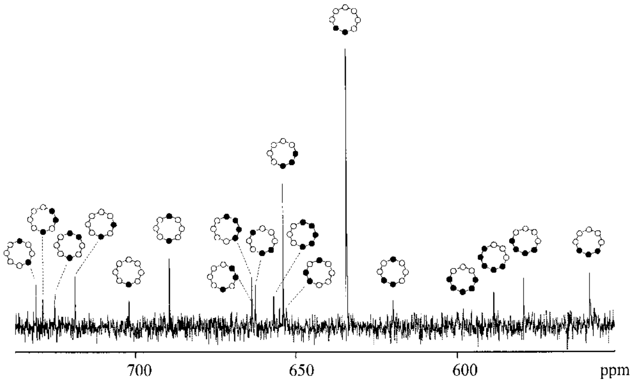

Figure 4. ^{77}Se NMR spectrum of a CS_2 solution of the mixture of selenium sulfides Se_nS_{8-n} ($n = 1-5$) formed from $SeCl_2$ and Ph_3PS: ○, S; ●, Se.

Reaction of $SeCl_2$ with Ph_3PE (E = S, Se). Formation of Selenium Sulfide Rings. In view of the facile formation of adducts of $SeCl_2$ with the sulfur ligands tmtu and tht we have also investigated the reactions of $SeCl_2$ with triphenylphosphine chalcogenides Ph_3PE (E = S, Se). The treatment of Ph_3PSe with $SeCl_2$ in CH_2Cl_2/THF produces Ph_3PCl_2 and an almost quantitative yield of elemental selenium (eq 4).

$$Ph_3PSe + SeCl_2 \rightarrow Ph_3PCl_2 + (^2/_x)Se_x \qquad (4)$$

The application of this procedure to Ph_3PS provides a mild route to eight-membered selenium sulfide rings Se_nS_{8-n} ($n = 1-5$), which were identified by ^{77}Se NMR spectroscopy (Figure 4). The assignments were made on the basis of previous data for the composition of sulfur−selenium melts containing ^{77}Se-enriched samples, which were investigated for melt compositions ranging from 10 to 40 mol % Se.[12b,23−25] There is remarkably good agreement between the ^{77}Se NMR chemical shifts found for the selenium sulfide rings produced from the reaction $SeCl_2$ and Ph_3PS and those reported for the corresponding rings in sulfur−selenium melts. The assignments are shown in Figure 4, and the relative abundances of selenium sulfides produced by the two different routes are compared in Table 7. The low abundance of SeS_7 compared to that of 1,2-Se_2S_6 is the most significant difference in the composition of selenium sulfides.

Table 7. ^{77}Se NMR Data for Selenium Sulfides, Se_nS_{8-n} ($n = 1-5$)

	$\delta(^{77}Se)^a$	rel abundance[c]	$\delta(^{77}Se)^b$	rel abundance[c]
SeS_7	701.0	6.0	699.7	40.0
1,2-Se_2S_6	633.9	35.9	633.9	20.0
1,3-Se_2S_6	718.4	4.8	716.9	2.5
1,4-Se_2S_6	730.1	6.6	729.1	2.0
1,5-Se_2S_6	688.5	6.3	687.3	3.5
1,2,3-Se_3S_5	654.3	17.6	654.2	10.5
	559.2		560.6	
1,2,4-Se_3S_5	728.5	3.1	727.4	4.0
	662.7		662.9	
	653.2		653.0	
1,2,5-Se_3S_5	724.6	9.6	723.7	3.5
	662.4		662.6	
	619.8		619.7	
1,2,3,4-Se_4S_4	664.1	5.9	664.4	5.5
	580.3		581.6	
1,2,3-Se_5S_3	657.5	4.2	657.9	3.0
	598.3		598.2	
	589.6		591.2	

[a] This work. [b] Reference 12c; these data refer to a selenium content of 40 mol % in sulfur−selenium melts, which were quenched and extracted with CS_2. [c] In mol %.

In both systems, for a given chemical composition, the isomer with juxtaposed selenium atoms is the most abundant. For Se_3S_5, however, the 1,2,5-isomer was found to be more abundant than the 1,2,4-isomer in this study. Finally, we note that Wynne et al. reported the formation of "Se_5S_3", identified on the basis of sulfur analysis from the decomposition of solutions of $SeCl_2$·tmtu in the presence of excess tmtu.[9] It seems likely that their product is also a mixture of selenium sulfides.

In summary, pure $SeCl_2$ is readily obtained by treatment of elemental selenium with an equimolar amount of SO_2Cl_2. It is stable *in THF* for 1 day at 23 °C and forms a crystalline bis-adduct with THT that may be stored in the solid state at −20 °C for weeks without decomposition. The THF solutions of $SeCl_2$ and the adduct $SeCl_2(tht)_2$ constitute potentially valuable Se(II) synthons for the development of selenium chemistry. In the reaction with triphenylphosphine sulfide $SeCl_2$ acts as a chlorinating agent leading to the generation of selenium sulfide rings under mild conditions.

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Supporting Information Available: An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) The composition of selenium sulfides in melts that were heated to ca. 430 °C and, subsequently, cooled to 135 °C has been shown to be approximately the same as that of melts that were cooled to room temperature and extracted with CS_2.

(24) Chivers, T.; Laitinen, R. S.; Schmidt, K. J. *Can. J. Chem.* **1992**, *70*, 719.

(25) For a review of selenium sulfides, see: Laitinen, R. S.; Pekonen, P.; Suontamo, R. J. *Coord. Chem. Rev.* **1994**, *130*, 1.