Inorg. Chem. **2005**, *44*, 4992–5000

Inorganic Chemistry

Article

Synthetic Applications of $(Me_3SiNSN)_2E$ (E = S, Se) in Chalcogen-Nitrogen Chemistry: Formation and Structural Characterization of Cl_2TeESN_2 (E = S, Se) and $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)X_4]$ (X = Cl, Br)

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Received February 19, 2005

The reaction of $(Me_3SiNSN)_2S$ with $TeCl_4$ in CH_2Cl_2 affords $Cl_2TeS_2N_2$ (**1**) and that of $(Me_3SiNSN)_2Se$ with $TeCl_4$ produces $Cl_2TeSeSN_2$ (**2**) in good yields. The products were characterized by X-ray crystallography, as well as by NMR and vibrational spectroscopy and EI mass spectrometry. The Raman spectra were assigned by utilizing DFT molecular orbital calculations. The pathway of the formation of five-membered Cl_2TeESN_2 rings by the reactions of $(Me_3SiNSN)_2E$ with $TeCl_4$ (E = S, Se) is discussed. The reaction of $(Me_3SiNSN)_2Se$ with $[PPh_4]_2[Pd_2X_6]$ yields $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)X_4]$ (X = Cl, **4a**; Br, **4b**), the first examples of complexes of the $(Se_2N_2S)^{2-}$ ligand. In both cases, this ligand bridges the two palladium centers through the selenium atoms.

Introduction

While the structural features and chemical properties of a large number of sulfur−nitrogen compounds are well-understood,[1–4] selenium−nitrogen and tellurium−nitrogen chemistry has seen rapid development only during recent years. Reagents such as trimethylsilyl chalcogen diamides, $[(Me_3Si)_2N]_2E$ (E = S, Se), have provided routes for selenium and tellurium-containing chalcogen-nitrogen compounds, for example, 1,5-$Se_2S_2N_4$,[5] Se_4N_4,[6] $[(Se_2SN_2)Cl]_2$,[7,8] $X_2TeSeSN_2$ (X = Cl, Br, I),[9] $X_2TeS_2N_2$ (X = Cl, Br),[9] $Cl_2Te_2SN_2$,[10] and $X_6Te_2SeN_2$ (X = Cl, Br).[11] Haas et al.[12–14] have shown that the treatment of $(OSN)_2E$ (E = S, Se) with $TeCl_4$ leads to novel tellurium-containing chalcogen-nitrogen compounds.

$(Me_3SiNSN)_2S$ can be prepared from $(Me_3SiN)_2S$ with SCl_2 and has been used as a starting material for the synthesis of S_4N_4.[15] We have recently reported that the analogous reaction utilizing $(Me_3SiN)_2S$ with $SeCl_2$ leads to the formation of $(Me_3SiNSN)_2Se$.[16] While its reaction with $SeCl_2$ produces 1,5-$Se_2S_2N_4$, that with SCl_2 affords an equimolar mixture of S_4N_4 and 1,5-$Se_2S_2N_4$. Interestingly, the reaction of $(Me_3SiNSN)_2S$ and $SeCl_2$ also yields a similar equimolar

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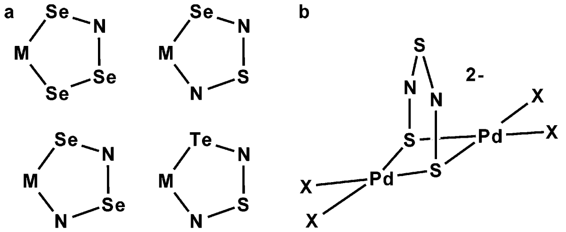
(1) Chivers, T. *Chem. Rev.* **1985**, *85*, 341.
(2) Chivers, T. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol. 2, p 793.
(3) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, *36*, 299.
(4) Wentrup, C.; Kampouris, P. *Chem. Rev.* **1991**, *91*, 363.
(5) Maaninen, A.; Laitinen, R. S.; Chivers, T.; Pakkanen, T. A. *Inorg. Chem.* **1999**, *38*, 3450.
(6) Siivari, J.; Chivers, T.; Laitinen, R. S. *Inorg. Chem.* **1993**, *32*, 1519.
(7) Wolmershäuser, G.; Brulet, C. R.; Street, G. B. *Inorg. Chem.* **1978**, *17*, 3586.
(8) Maaninen, A.; Konu, J.; Laitinen, R. S.; Chivers, T.; Schatte, G.; Pietikäinen, J.; Ahlgren, M. *Inorg. Chem.* **2001**, *40*, 3539.
(9) Haas, A.; Pryka, M.; Schäfers, M. *Chem. Ber.* **1994**, *127*, 1865.
(10) Haas, A.; Kasprowski, J.; Pryka, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1144.
(11) Haas, A.; Schäfers, M. *Chem. Ber.* **1995**, *128*, 437.
(12) Haas, A.; Kasprowski, J.; Pryka, M. *Chem. Ber.* **1992**, *125*, 789.
(13) Haas, A.; Pryka, M. *Chem. Ber.* **1995**, *128*, 11.
(14) Haas, A.; Kasprowski, J.; Pryka, M. *Chem. Ber.* **1992**, *125*, 1537.
(15) Lidy, W.; Sundermeyer, W.; Verbeek, W. *Z. Anorg. Allg. Chem.* **1974**, *406*, 228.
(16) Konu, J.; Maaninen, A.; Paananen, K.; Ingman, P.; Laitinen, R. S.; Chivers, T.; Valkonen, J. *Inorg. Chem.* **2002**, *41*, 1430.

10.1021/ic050261f CCC: $30.25

Scheme 1



mixture. These reactions presumably proceed via cyclic four-membered intermediates.[16] The reactions of chalcogen diimides or diamides with tellurium halides provide obvious routes to many chalcogen-nitrogen species. In This Paper, we report the formation of $Cl_2TeS_2N_2$ (**1**) together with small amounts of $S_4N_4{\cdot}TeCl_4$ (**3**)[17] by the reaction of $(Me_3SiNSN)_2S$ with $TeCl_4$. Similarly, the reaction of $(Me_3SiNSN)_2Se$ with $TeCl_4$ affords $Cl_2TeSeSN_2$ (**2**) as the main product.

The above considerations concerning metal-free heavy chalcogen-nitrogen systems also generally apply to metal complexes of heavy chalcogen-nitrogen anions. Thus, the first examples of complexes of Se–N anions were only isolated many decades after the first metal sulfur–nitrogen complexes. Since then, however, several examples of systems containing combinations of chalcogens have been reported. In general, all such complexes are based on one fundamental unit, namely, a five-membered metallacycle containing the $[S_3N]^-$ or $[S_2N_2]^{2-}$ ligands (or the protonated analogue of the latter, i.e., $[S_2N_2H]^-$). Complexes of $[Se_3N]^-$,[18] $[Se_2N_2]^{2-}$,[19] $[SeSN_2]^{2-}$,[20] and $[TeSN_2]^{2-}$[21] together with the protonated forms of the latter three are all known (Scheme 1a).

Synthons used in the preparation of these species are limited in number and include the binary Se_4N_4,[18,19] which is difficult to handle because of its shock sensitivity. Indeed, in some cases the anions are actually generated in situ during reactions in liquid ammonia.[19] This lack of potential reagents is one of the reasons for the slow development of complexes containing heavy chalcogen analogues of larger S–N binary ligand systems such as $[S_2N_3]^-$ [22,23] and $[S_4N_4]^{2-}$.[24,25] One source of the former species is S_5N_6,[22] for which there is no selenated analogue, and the reactions of Se_4N_4 invariably appear to result in the four-membered anions rather than the putative $[Se_4N_4]^{2-}$ ligand.[18,19] The most pertinent of the larger sulfur–nitrogen ligands to this study is $[S_3N_2]^{2-}$, which can act as a bridging ligand between metal centers.[23,26] Its formation in the reaction of $(Me_3SiNSN)_2S$ with salts of $[Pd_2X_6]^{2-}$ (X = Cl, Br) (Scheme 1b)[23] raises the obvious question as to the reactivity of $(Me_3SiNSN)_2Se$ toward these halobridged palladium species. Here, we report on such reactions and show complexes of the new mixed anion $[Se_2SN_2]^{2-}$ that is the first example of a selenium-substituted five-membered chalcogen-nitrogen anion. X-ray crystallography confirms the nature of this new ligand and reveals it to coordinate to the palladium atoms via the two bridging selenium atoms.

Experimental Section

General Procedures. All reactions and manipulations of air- and moisture-sensitive reagents were carried out under an argon atmosphere passed through P_4O_{10}. SCl_2, SO_2Cl_2, and $TeCl_4$ (Aldrich) were used without further purification. $[(Me_3Si)_2N]_2S$ was prepared from $(Me_3Si)_2NH$ by utilizing the method of Wolmershäuser et al.[7] and was purified by distillation. $(Me_3SiNSN)_2S$ and $(Me_3SiNSN)_2Se$ were prepared from $[(Me_3Si)_2N]_2S$ by the procedures described earlier.[15,16,23] The salts $[PPh_4]_2[Pd_2X_6]$ (X = Cl or Br) were prepared as reported previously.[26] Hexane and THF were dried by distillation over Na/benzophenone and dichloromethane over P_4O_{10} under a nitrogen atmosphere prior to use.

Spectroscopy. The ^{13}C, ^{14}N, ^{77}Se, and ^{125}Te NMR spectra of the reaction solutions of $(Me_3SiNSN)_2E$ (E = S, Se) with $E'Cl_4$ (E′ = Se, Te) were recorded in dichloromethane and in THF on a Bruker DPX 400 spectrometer operating at 100.62, 28.909, 76.406, and 126.240 MHz, respectively, and the ^{1}H NMR spectra of the reaction solutions of $(Me_3SiNSN)_2Se$ with $[PPh_4]_2[Pd_2X_6]$ (X = Cl, Br) were recorded on a Bruker AC250 spectrometer. The spectral widths were 30.30, 14.49, 99.01, and 95.24 kHz for ^{13}C, ^{14}N, ^{77}Se, and ^{125}Te, respectively, yielding the respective resolutions of 0.62, 7.08, 1.51, and 1.45 Hz/data point. The pulse widths were 4.0 μs for ^{13}C, 12.0 μs for ^{14}N, 6.70 μs for ^{77}Se, and 6.67 μs for ^{126}Te, corresponding to nuclear tip angles of 33, 44, 46, and 30°, respectively. The ^{13}C accumulations contained ca. 200 transients,^{14}N accumulations ca. 25 000 transients, ^{77}Se accumulations ca. 20 000 transients, and ^{125}Te accumulations 9000–18 000 transients. All spectra were recorded unlocked. The ^{13}C NMR chemical shifts are reported relative to $(CH_3)_4Si$ and the ^{14}N NMR chemical shifts relative to CH_3NO_2. All ^{77}Se NMR spectra are referenced externally to a saturated solution of SeO_2 in D_2O and ^{125}Te NMR spectra to a saturated solution of H_6TeO_6. The ^{77}Se chemical shifts are reported relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$] and ^{125}Te chemical shifts relative to Me_2Te [$\delta(Me_2Te) = \delta(H_6TeO_6) + 712$].

MS-EI mass spectra of **1** and **2** were recorded by using a Micromass Quattro II spectrometer at 70 eV of electron energy.

The Raman spectra of **1** and **2** were recorded from solid samples at room temperature by using a Bruker IFS-66 spectrometer equipped with an FRA-16 Raman unit and Nd:YAG laser (power 110 mW; 8–64 scans; spectral resolution ±1 cm^{-1}; Blackmann–Harris four-term apodization, no white light correction; scattering geometry 180°). IR spectra of **4a** and **4b** were recorded on a Perkin-Elmer 2000 spectrometer.

Reactions of $(Me_3SiNSN)_2E$ (E = S, Se) with $TeCl_4$. $(Me_3SiNSN)_2S$ (0.149 g, 0.50 mmol) or $(Me_3SiNSN)_2Se$ (0.172 g, 0.5 mmol) was dissolved in dichloromethane (20 mL). In both reactions, the resulting solution was added to a suspension of $TeCl_4$ (0.135 g, 0.50 mmol) in dichloromethane (10 mL) at −80 °C. The reaction

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[17] The full characterization of **3** will be published elsewhere.

[18] Jones, R.; Kelly, P. F.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1989**, 408.

[19] Kelly, P. F.; Parkin, I. P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1047.

[20] Kelly, P. F.; Parkin, I. P.; Sheppard, R. N.; Woollins, J. D. *Heteroatom. Chem.* **1991**, *2*, 301.

[21] Kelly, P. F.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Polyhedron* **1990**, *9*, 2659.

[22] Kelly, P. F.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 616.

[23] Kelly, P. F.; Slawin, A. M. Z.; Soriano-Rama, A. *J. Chem. Soc., Dalton Trans.* **1996**, 53.

[24] Edelmann, F.; Roesky, H. W.; Spang, C.; Noltemeyer, M.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 931.

[25] Kelly, P. F.; Sheppard, R. N.; Woollins, J. D. *Polyhedron* **1992**, *11*, 2605.

[26] Ginn, V. C.; Kelly, P. F.; Slawin, A. M. Z.; Williams, D. J.; Woollins J. D. *J. Chem. Soc., Dalton Trans.* **1992**, 963.

Table 1. Crystal Data and Structure Refinement for $Cl_2TeS_2N_2$ (**1**), $Cl_2TeSeSN_2$ (**2**), $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)Cl_4]$ (**4a**), and $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)Br_4]$ (**4b**)

	1	**2**	**4a**	**4b**
empirical formula	$Cl_2N_2S_2Te$	Cl_2N_2SSeTe	$C_{48}H_{40}Cl_4N_2P_2Pd_2SSe_2$	$C_{48}H_{40}Br_4N_2P_2Pd_2SSe_2$
fw, g/mol	290.64	337.54	1251.34	1429.18
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$C2/c$	Pbca	$P2_1/c$	$P2_1/c$
a, Å	19.8796(7)	8.352(2)	9.6484(6)	9.9248(4)
b, Å	8.7884(3)	7.953(2)	34.684(2)	34.890(1)
c, Å	7.2922(3)	19.853(4)	14.6209(9)	14.6325(6)
β, deg	96.234(2)	90.00	97.824(2)	97.255(2)
V, Å^3	1266.49(8)	1318.7(5)	4847.3(5)	5026.3(3)
Z	8	8	4	4
T, °C	−150(2)	−120(2)	−120(2)	−120(2)
ρ_{calcd}, g/cm^3	3.049	3.400	1.715	1.889
μ (Mo Kα), mm^{-1}	6.076	11.039	2.609	5.484
crystal size	0.25 × 0.25 × 0.05	0.20 × 0.20 × 0.10	0.41 × 0.05 × 0.03	0.56 × 0.18 × 0.12
F(000)	1056	1200	2464	2752
θ range, deg	2.54−27.48	2.05−24.98	1.52−25.00	1.52−25.00
reflns collected	7018	13311	23365	36596
unique reflns	1439	1150	8544	8842
R_1 $[I > 2\sigma(I)]^a$	0.0235	0.0415	0.0347	0.0250
wR_2 (all data)	0.0573^b	0.1260^c	0.0737^d	0.0555^e
GOF on F^2	1.220	1.190	1.053	1.021

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. [b] $w = [\sigma^2(F_o^2) + (0.0200P)^2 + 4.0000P]^{-1}$. [c] $w = [\sigma^2(F_o^2) + (0.0597P)^2 + 31.6007P]^{-1}$. [d] $w = [\sigma^2(F_o^2) + (0.0223P)^2 + 8.6937P]^{-1}$. [e] $w = 1/[\sigma^2(F_o^2) + (0.0214P)^2 + 6.6340P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

mixtures were stirred overnight and were allowed to warm slowly to room temperature. In both cases, a reddish solution and a red-bown precipitate were obtained. The precipitates were identified as $Cl_2TeS_2N_2$ (**1**) (0.047 g, 32% on the basis of the initial amount of tellurium) in the case of the reaction involving $(Me_3SiNSN)_2S$ and $Cl_2TeSeSN_2$ (**2**) (0.081 g, 48% on the basis of the initial amount of tellurium) in the case of the reaction involving $(Me_3SiNSN)_2Se$. Further crystallization from the remaining reaction solution (CH_2Cl_2) at room temperature afforded red-brown plates of $Cl_2TeS_2N_2$ (**1**) from the former reaction and red plates of $Cl_2TeSeSN_2$ (**2**) from the latter reaction. In addition, the former reaction also produced a small amount of red crystals of $S_4N_4{\cdot}TeCl_4$ (**3**).[17] All products were characterized by vibrational, NMR, and mass spectrometry as well as by X-ray crystallography. $Cl_2TeS_2N_2$ (**1**): NMR (THF, 25 °C, δ): ^{14}N −79, −121;[27] ^{125}Te 2110. MS [EI m/z (I_{rel})]: 46(100) NS^+, 78(15) NS_2^+, 92(30) $N_2S_2^+$, 130(86) Te^+, 144(11) NTe^+, 165(52) $ClTe^+$, 176(55) $NSTe^+$, 200(40) Cl_2Te^+, 211(32) $NSClTe^+$, 222(34) $N_2S_2Te^+$, 246(37) $NSCl_2Te^+$, 257(81) $N_2S_2ClTe^+$, 292(23) $N_2S_2Cl_2Te^+$. $Cl_2TeSeSN_2$ (**2**): NMR (THF, 25 °C, δ): ^{14}N −79, −108;[27] ^{77}Se 1195; ^{125}Te 1973. MS [EI m/z (I_{rel})]: 46(100) NS^+, 80(49) Se^+, 94(62) NSe^+, 130(73) Te^+, 140(11) N_2SSe^+, 144(10) NTe^+, 165(45) $ClTe^+$, 176(42) $NSTe^+$, 200(40) Cl_2Te^+, 208(19) $SeTe^+$, 222(52) $NSeTe^+$, 246(24) $NSCl_2Te^+$, 257(47) $NClSeTe^+$, 268(57) N_2SeTe^+, 292(24) NCl_2SeTe^+, 303(65) $N_2SClSeTe^+$, 338(14) $N_2SCl_2SeTe^+$.

Reactions of $(Me_3SiNSN)_2Se$ with $[PPh_4]_2[Pd_2X_6]$ [X = Cl (4a), Br (4b)]. 4a. A solution of $[PPh_4]_2[Pd_2Cl_6]$ (0.200 g, 0.18 mmol) in dry CH_2Cl_2 (60 mL) was treated with solid $(Me_3SiNSN)_2Se$ (0.125 g, 0.36 mmol), added with vigorous stirring. The resulting solution immediately started to darken in color from light orange to dark red and a cloudiness developed within a minute of the start of reaction. After 48 h stirring, the mixture consisted of a dark brown precipitate within a dark red solution. After filtration and reduction of the solution volume to ca. 20 mL in vacuo, ether vapor diffusion over many days afforded dark orange crystals of **4a** (0.106 g, 47% on the basis of Pd). **4a**: IR (cm^{-1}): Bands due to $[PPh_4]^+$ plus 1054 (w), 872 (w), 856 (w), 846 (w), 634 (m), 326 (mw), 307 (m), 297 (m). Anal. Calcd. for $C_{48}H_{40}Cl_4N_2P_2Pd_2SSe_2$: C 40.7, H 1.7, N 2.0; found: C 40.1, H 2.3, N 1.8.

The preparation of **4b** was performed in an identical manner to that generating **4a**. $[PPh_4]_2[Pd_2Br_6]$ (0.200 g, 0.15 mmol) was treated with $(Me_3SiNSN)_2Se$ (0.100 g, 0.30 mmol). In this case, the dark wine-red color of the reaction mixture lightened with time; after 48 h, small amounts of orange precipitate were observed. Crystallization as before yielded dark orange crystals of **4b** (0.124 g, 58% on the basis of Pd). **4b**: IR (cm^{-1}): Bands due to $[PPh_4]^+$ plus 1028 (w), 858 (w), 847 (w), 834 (w), 596 (m), 363 (m), 221 (m), 209 (m). Anal. Calcd. for $C_{48}H_{40}Br_4N_2P_2Pd_2SSe_2$: C 39.8, H 2.6, N 1.7; found: C 40.3, H 2.8, N 2.0.

X-ray Crystallography. Crystal data for $Cl_2TeS_2N_2$ (**1**), $Cl_2TeSeSN_2$ (**2**),[30] $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)Cl_4]$ (**4a**), and $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)Br_4]$ (**4b**) are given in Table 1. Diffraction data were collected with a Nonius Kappa CCD diffractometer for **1** and **2** and with a Bruker SMART AXS 1000 CCD diffractometer for **4a** and **4b** using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) in both cases. The data were corrected for Lorentz and

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(27) In reaction 1, ^{14}N NMR spectra of the THF solutions also showed signals for S_4N_4 (δ = −256 ppm) [28] and NH_4Cl (δ = −361 ppm)[29] in addition to the product resonances. The resonance due to S_4N_4 is repeatedly observed already in the ^{14}N NMR spectra of the reaction solutions, but NH_4Cl is detected only after prolonged standing of the sample in THF in the NMR tube. It is probable that NH_4Cl is formed by the decomposition of the product because of moisture in the solvent or because the solvent itself initiates decomposition. To verify this interpretation, the reaction of $(Me_3SiNSN)_2S$ with $TeCl_4$ was carried out in CS_2, and the precipitate was dissolved in THF followed by the recording of the ^{14}N NMR spectrum. Also in this case, NH_4Cl was detected in the NMR spectrum upon standing. The ^{13}C NMR spectra of reaction solutions of reaction 1 in CH_2Cl_2 showed only one resonance for Me_3SiCl excluding the unlikely possibility of Me groups being the proton source for the formation of NH_4Cl. This indicates that the proton source for the formation of NH_4Cl is indeed either THF or moisture in THF and that NH_4Cl is the decomposition product of Cl_2TeESN_2 rather than a byproduct of reaction 1.

(28) Chivers, T.; Oakley, R. T.; Scherer, O. J.; Wolmershäuser, G. *Inorg. Chem.* **1981**, *20*, 914.

(29) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1990**, *29*, 1251.

(30) The crystal structure of **2** has been reported at room temperature by Haas et al.[12] We have redetermined the crystal structure of **2** to identify the product obtained from reaction 2 and to be able to compare the bond parameters of **1** and **2** at low temperatures. The general structural features of **2** at low temperatures are similar to those at room temperature[12] (see Figure 3).

polarization effects, and an empirical absorption correction was applied to the net intensities. The structures **1** and **2** were solved by direct methods using SHELXS-97[31] and were refined using SHELXL-97.[32] The structures **4a** and **4b** were solved and refined by using programs Bruker SMART,[33] SAINT,[33] SHELXTL,[34] and local programs. The scattering factors for the neutral atoms were those incorporated with the programs.

Computational Details. Ab initio MO calculations of Cl_2TeESN_2 (E = S, Se) were carried out using the Stuttgart relativistic large core effective core potential approximation (RLC ECP)[35−37] by augmenting the double-ζ quality basis sets of the valence orbitals by two polarization functions for all atoms. Fundamental vibrations and the geometry optimization of **1** and **2** were calculated at the DFT level of theory involving Becke's three-parameter hybrid functionals with the Perdew/Wang 91 correlation (B3PW91).[38−44] The calculated wavenumbers were scaled by 0.993 to eliminate the systematic errors.[45] The calculations for geometry optimizations and fundamental vibrations were also performed at the same level of theory with DZVP[46] basis set which takes into account all electrons of the atoms. In both cases, an excellent correlation between the calculated and observed wavenumbers was achieved. Calculations were performed with the GAUSSIAN 03 (Rev. B.04) program.[47]

Results and Discussions

Reactions of $(Me_3SiNSN)_2E$ with $TeCl_4$ (E = S, Se).[48,49] The reaction of $(Me_3SiNSN)_2S$ with $TeCl_4$ in CH_2Cl_2 affords $Cl_2TeS_2N_2$ (**1**) in ca. 32% yield. The reaction also produces N_2, Me_3SiCl, and S_4N_4 (eq 1). Some S_4N_4 subsequently reacts with $TeCl_4$ yielding a small amount of $S_4N_4{\cdot}TeCl_4$ (**3**).[17]

$$(Me_3SiNSN)_2E + TeCl_4 \rightarrow Cl_2TeESN_2 + 2Me_3SiCl + {}^1/_2N_2 + {}^1/_4S_4N_4 \quad (1)$$

In an analogous manner, $(Me_3SiNSN)_2Se$ reacts with $TeCl_4$ producing $Cl_2TeSeSN_2$ (**2**) in ca. 48% yield (eq 1). In this reaction, we did not observe the formation of $S_4N_4{\cdot}TeCl_4$ (**3**).

The EI mass spectra of both the initial reaction precipitate and the crystallized product from the decanted solutions formed in the reactions of both $(Me_3SiNSN)_2S$ and $(Me_3SiNSN)_2Se$ with $TeCl_4$ exhibited the molecular ions of **1** and **2** ($Cl_2TeS_2N_2^+$, and $Cl_2TeSeSN_2^+$), respectively, as fragments of highest mass. A reasonable fragmentation pattern was also observed for both compounds. The fragments were unambiguously assigned by consideration of isotopic distributions. The calculated isotopic distributions of the molecular ions of **1** and **2** as well as their fragments agree well with the observed isotopic distribution patterns. The fragmentation patterns are consistent with those proposed by Haas et al.[9,12]

The ^{14}N and ^{125}Te NMR spectra of **1** and **2** were recorded in THF. The ^{14}N NMR spectrum of **1** shows four signals at −79, −121, −256, and −361 ppm and that of **2** shows four resonances at −79, −108, −256, and −361 ppm. In both cases, the first two signals are assigned to the five-membered Cl_2TeESN_2 (E = S, Se) rings (−79 and −121 ppm for **1** and −79 and −108 ppm for **2**) and the latter two resonances are assigned to S_4N_4 (−256 ppm) and NH_4Cl (−361 ppm).[27] The ^{14}N chemical shifts of **1** and **2** are reasonable for the five-membered TeS_2N_2-rings containing a N=S=N fragment.[50] The ^{125}Te spectrum of **1** shows a single resonance at 2110 ppm and that of **2** exhibits a single resonance at 1973 ppm, These two resonances show expected relative values, since the replacement of the selenium atom with a more electronegative sulfur atom in the five-membered equatorial ring can be considered to cause deshielding of the adjacent tellurium atom. However, Haas et al.[9] reported a ^{125}Te chemical shift of 1764 ppm for **1** recorded in THF/C_6D_6 (1:1). The ^{77}Se NMR spectrum of **2** exhibits a single resonance at 1195 ppm.

The Raman spectra of crystalline **1** and **2** are shown in Figure 1.[51] The assignment of the observed fundamental vibrations of $Cl_2TeS_2N_2$ (**1**) is based on the B3PW91

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

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

(33) *SMART and SAINT software for CCD diffractometers*; Bruker AXS, Inc.: Madison, WI, 1994.

(34) Sheldrick, G. M. *SHELXTL, User Manual*, Version 5; Bruker AXS, Inc.: Madison, WI, 1994.

(35) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245.

(36) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(37) Buhl, M.; Thiel, W.; Fleischer, U.; Kutzelnigg, W. *J. Phys. Chem.* **1995**, *99*, 4000.

(38) Becke, A. D. *J. Phys. Chem.* **1993**, *98*, 5648.

(39) Burke, K.; Perdew, J. P.; Wang, Y. In *Electron Density Functional Theory: Recent Progress and New Directions*; Dobson, J. F., Vignale, G., Das, M. P., Eds.; Plenum: New York, 1998.

(40) Perdew, J. P. In *Electronic Structure of Solids*; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991.

(41) Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B45*, 13244.

(42) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev.* **1992**, *B46*, 6671.

(43) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev.* **1993**, *B48*, 4978.

(44) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev.* **1996**, *B54*, 16553.

(45) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(46) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

(47) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M., Gill; P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 03*, Revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(48) Haas et al.[9] have reported that the reaction of $[(Me_3Si)_2N]_2S$ with $TeCl_4$ and SCl_2 in CH_2Cl_2 also produces $Cl_2TeS_2N_2$. Although the characterization of their product was incomplete, we believe that this reaction indeed affords **1**.

(49) Haas et al. have reported the preparation of **2** by the reactions of $Se(NSO)_2$ with $TeCl_4$[12] and $[(Me_3Si)_2N]_2S$ with $TeCl_4$ and $SeCl_4$.[9]

(50) $Cl_2SeS_2N_2$[29] that also contains the N=S=N fragment has been reported to exhibit two ^{14}N resonances at −51.7 and −137.8 ppm. The ionic nature of the five-membered ring and the higher electronegativity of sulfur and selenium compared to that of tellurium may explain the minor differences in chemical shifts.

(51) Raman spectrum was recorded both from the reaction precipitate and from the crystals to verify the identity of the products.

Table 2. Fundamental Vibrations (cm^{-1}) of $Cl_2TeS_2N_2$ (**1**) and $Cl_2TeSeSN_2$ (**2**)

$Cl_2TeS_2N_2$ (**1**)								$Cl_2TeSeSN_2$ (**2**)							
obs.	I[a]	ECP[b]	I[c]	DZVP[d]	I[e]		assignment[f]	obs.	I[a]	ECP[b]	I[c]	DZVP[d]	I[e]		assignment[f]
1022	vw	1061	10	1064	16	a′	ν_{SN} 73 ν_{TeN} 10	1034	vw	1068	7	1072	12	a′	ν_{SN} 56 ν_{SeN} 15 ν_{TeN} 11
								1021	vw						
943	w	959	32	959	40	a′	ν_{SN} 65 ν_{TeN} 15	943	w	965	43	962	57	a′	ν_{SN} 52 ν_{TeN} 15 ν_{SeN} 13
								687	vw						
689	vw	700	9	707	8	a′	ν_{SN} 58 δ_{SNS} 19	609	vw	607	10	614	10	a′	ν_{SeN} 31 δ_{SeNS} 21 δ_{NSN} 18
603	vw	603	6	599	5	a′	ν_{TeN} 25 δ_{NSN} 21 $\delta_{TeN\,S}$ 20 δ_{SNS} 11	560	vw	580	3	570	3	a′	ν_{TeN} 29 δ_{TeNS} 20 ν_{SeN} 14 ν_{SN} 12
502	m	511	41	503	44	a′	ν_{TeN} 31 δ_{SNS} 18 ν_{SN} 12								
								489	w						265 + 225
								430	m	454	41	443	38	a′	ν_{TeN} 31 ν_{SeN} 19 δ_{SeNS} 12 δ_{NSN} 10
361	vw	325	1	325	1	a″	τ 84								
								347	vw						225 + 122
333	m	319	18	320	20	a′	ν_{TeS} 27 $\delta_{TeS\,N}$ 16 ν_{TeN} 14 δ_{SNS} 10	332	w	326	1	324	1	a″	τ 82
		289	2	296	1	a″	τ 50 ν_{TeCl} 40			286	3	292	1	a″	τ 51 ν_{TeCl} 43
268	vs	271	100	271	100	a′	ν_{TeCl} 65 ν_{TeS} 11	299	vs	269	10 0	268	10 0	a′	ν_{TeCl} 75
		265	1	269	1	a″	τ 79 $\delta_{ClTe\,N}$ 12	265	w	247	10	248	12	a′	δ_{TeSeN} 15 δ_{NTeSe} 13 δ_{TeNS} 11 δ_{SeNS} 11
244	s	246	24	244	29	a′	ν_{TeS} 36 ν_{TeCl} 15 τ 11	245	w	244	2	242	4	a″	τ 80 δ_{ClTeN} 13
								225	vs	195	23	200	24	a′	ν_{TeSe} 40
189	vw							148	m						
139	s							122	m						
112	vs	110	16	118	21	a″	τ 60 $\delta_{ClTe\,S}$ 23 $\delta_{ClTe\,N}$ 13	107	s	88	7	97	6	a′	τ 36 δ_{ClTeN} 25 δ_{ClTeCl} 10
102	vs	89	7	99	6	a′	τ 46 $\delta_{ClTe\,N}$ 20 $\delta_{ClTe\,S}$ 14	92	m	86	15	91	18	a″	τ 57 δ_{ClTeSe} 25 δ_{ClTeN} 10
70	vw	64	15	66	18	a″	τ 84			64	4	74	3	a′	τ 33 δ_{ClTeSe} 20 δ_{ClTeCl} 24 δ_{ClTeN} 12
		63	2	73	2	a′	τ 55 $\delta_{ClTe\,S}$ 19 $\delta_{ClTe\,N}$ 14			63	16	62	18	a″	τ 85

[a] Observed relative intensity. [b] Calculated wavenumbers at B3PW91/ECP level of theory. [c] Calculated Raman intensities at B3PW91/ECP level of theory. [d] Calculated wavenumbers at B3PW91/DZVP level of theory. [e] Calculated Raman intensities at B3PW91/DZVP level of theory. [f] Assignments are based on B3PW91/DZVP level of theory.

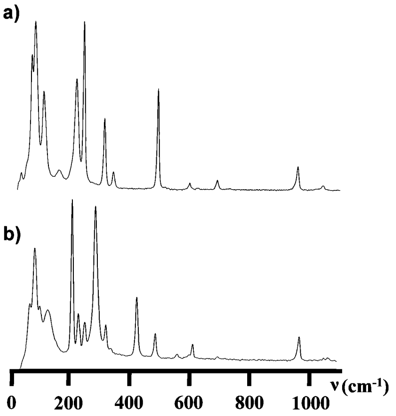

Figure 1. The Raman spectra of **1** and **2** [a and b, respectively].

calculations of the vibrational frequencies and intensities and is shown in Table 2. Both Cl_2TeESN_2 (E = S, Se) species belong to the point group C_s and therefore all 15 fundamental vibrations are Raman active in both cases. It can be seen from Table 2 that the wavenumbers and intensities of the calculated fundamental vibrations agree well with the observed Raman lines both at B3PW91/RLC ECP and B3PW91/DZVP level of theory. The main contributions to the potential energy are indicated at the B3PW91/DZVP level of theory. They are in close agreement with those calculated at B3PW91/RLC ECP level.

Crystal Structures of Cl_2TeESN_2 (E = S, Se). The structure of $Cl_2TeS_2N_2$ (**1**) with the atomic numbering scheme is shown in Figure 2. The molecule consists of a planar five-membered ring with the tellurium atom bonded to two exocyclic chlorine atoms. Unlike analogous $Cl_2TeSeSN_2$ (**2**) (Figure 3),[30] the structure of **1** shows no Te···N close contacts, but there are three Te···Cl secondary bonds between the neighboring molecules.

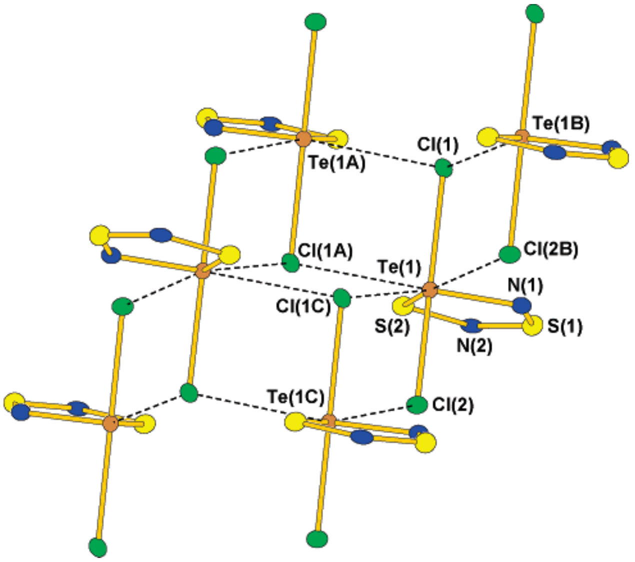

Figure 2. The structure of $Cl_2TeS_2N_2$ (**1**) showing the two parallel chains linked with Te···Cl close contacts. Thermal ellipsoids are drawn at the 50% probability level. Symmetry operations: A: −*x*, *y*, 0.5 − *z*. B: *x*, 1 − *y*, 0.5 + *z*. C: *x*, 1 − *y*, *z* − 0.5.

The relevant bond parameters of **1** and **2** are summarized in Table 3. The S−N bond lengths in the NSN fragment of **1** [1.542(3) and 1.583(3) Å] are similar to those in **2** [1.543(9)−1.558(9) Å] and indicate double bond character.[52] The corresponding bonds in $(ClTeS_2N_2)_2(Cl)[AsF_6)]$ [1.53(1)−1.57(1) Å],[9] $(ClTeSeSN_2)[AsF_6]$ [1.54(1) Å],[10] and $Cl_2SeS_2N_2$ [1.540(7)−1.550(7) Å][29] are also in close agreement. The Te−N bond length [2.038(3) Å] in **1** is shorter than the single

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(52) The S═N double bond length of 1.516(6) Å is observed in $(ONS)_2Se$[53] by X-ray crystallography and that of 1.536(3) Å is observed in $Me_3SiN{=}S{=}NSiMe_3$[54] by electron diffraction. The S−N single bond length of 1.716(3) Å is exhibited by $(Me_3Si)_2N{-}S{-}N(SiMe_3)_2$.[55]

Table 3. Selected Bond Parameters for $Cl_2TeS_2N_2$ (**1**) and $Cl_2TeSeSN_2$ (**2**)

	1	2		1	2
S(1)−N(1)	1.542(3)	1.558(9)	Te(1)−Cl(2)	2.4894(9)	2.770(2)
S(1)−N(2)	1.583(3)	1.543(9)	Te(1)···Cl(1A)	3.0393(8)[c]	3.568(3)[f]
Te(1)−N(1)	2.038(3)	1.994(8)	Te(1)···Cl(2B)	3.2266(9)[d]	2.925(3)[g]
E−N(2)	1.618(3)[a]	1.781(9)[b]	Te(1)···Cl(1C)	3.6360(8)[e]	
Te(1)−E	2.4316(8)[a]	2.531(1)[b]	Te(1)···(N1C)		3.171(8)[h]
Te(1)−Cl(1)	2.6380(9)	2.418(2)			
N(1)−S(1)−N(2)	115.2(2)	115.2(5)	N(1)−Te(1)−Cl(1)	90.63(8)	88.4(2)
S(1)−N(1)−Te(1)	115.9(2)	119.2(5)	N(1)−Te(1)−Cl(2)	89.48(8)	85.0(2)
S(1)−N(2)−E	121.9(2)[a]	122.6(5)[b]	E−Te(1)−Cl(1)	90.09(3)[a]	94.05(7)[b]
N(1)−Te(1)−E	87.20(8)[a]	88.1(2)[b]	E−Te(1)−Cl(2)	90.43(3)[a]	86.72(6)[b]
N(2)−E−Te(1)	99.4(1)[a]	94.6(3)[b]	Cl(1)−Te(1)−Cl(2)	179.48(3)	173.31(8)

[a] E = S(2). [b] E = Se(1). [c] −*x*, *y*, 0.5 − *z*. [d] *x*, 1 − *y*, 0.5 + *z*. [e] *x*, 1 − *y*, *z* − 0.5. [f] 0.5 − *x*, *y* − 0.5, *z*. [g] 0.5 − *x*, *y* + 0.5, *z*. [h] 1 − *x*, −*y*, −*z*.

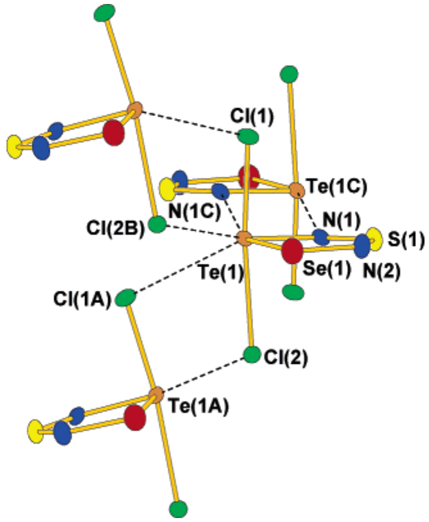

Figure 3. The structure of $Cl_2TeSeSN_2$ (**2**) showing one Te···N and two Te···Cl close contacts. Thermal ellipsoids are drawn at the 50% probability level. Symmetry operations: A: 0.5 − *x*, *y* − 0.5, *z*. B: 0.5 − *x*, *y* + 0.5, *z*. C: 1 − *x*, −*y*, −*z*.

bond length[56] being close to those in $[(Me_3Si)_2N]_2Te$ [2.045(2) and 2.053(2) Å][58] and $Te(NSO)_2$ [2.039(7) Å].[59] It is somewhat longer than the Te−N bonds in the cationic species $(ClTeS_2N_2)_2(Cl)[AsF_6]$ [1.972(7)−1.987(8) Å][9] and $(ClTeTeSeSN_2)[AsF_6]$ [2.00(1) Å].[10] Interestingly, it is also slightly longer than the Te−N bond of 1.994(8) Å in $Cl_2TeSeSN_2$.

The S(2)−N(2) bond [1.618(3) Å] in **1** is somewhat shorter than the single bond of 1.716(3) Å in $[(Me_3Si)_2N]_2S$[55] and is also slightly shorter than the corresponding S−N bonds in the cation of $(ClTeS_2N_2)_2(Cl)[AsF_6]$ [1.652(7) and 1.63(1) Å][9] and $[(S_3N_2)Cl]_2$ [1.618(3) and 1.642(4) Å].[60] The Te−S bond [2.4316(8) Å] is close to the sum of the covalent radii for tellurium and sulfur (2.41 Å)[57] and is also near to the bond lengths of 2.420(4) and 2.411(4) Å found in $(ClTeS_2N_2)_2(Cl)[AsF_6]$,[9] indicating a single bond length. The Te−Cl(1) and Te−Cl(2) bond lengths [2.6380(9) and 2.4894(9) Å, respectively] are significantly longer than the sum of the covalent radii for tellurium and chlorine (2.36 Å)[57] but are relatively close to the bond lengths of 2.770(2) and 2.418(2) Å found in $Cl_2TeSeSN_2$. The lengthening of these bonds is due to the intermolecular Te···Cl close contacts.

The two intermolecular Te···Cl close contacts [3.0393(8) and 3.2266(9) Å] are significantly shorter than the sum of the van der Waals radii of 4.01 Å[57] for tellurium and chlorine and link the adjacent molecules into two parallel chains (Figure 2). In addition, the structure includes a third Te···Cl close contact that is weaker than the other two [3.6360(8) Å]. These three Te···Cl close contacts expand the coordination number of the tellurium atom to seven. This is a typical example of the concept of secondary bonding interaction that has been introduced by Alcock.[61]

Formation of Cl_2TeESN_2 (E = S, Se). Haas et al.[62] have reported that the condensation of TeX_4 (X = F, Cl) with $(Me_3SiNSN)_2S$ affords eight-membered ring molecules $[X_2Te(\mu\text{-}NSN)_2S]$ (X = F, Cl) as a result of the cleavage of Si−N bonds and the elimination of Me_3SiCl followed by a ring closure. We have recently reported that the reactions of $(Me_3SiNSN)_2E$ and $E'Cl_2$ (E, E′ = S or Se) involve a cleavage of the E−N bond in the middle of the NSN−E−NSN chain yielding eight-membered cage compounds ($EE'S_2N_4$) possibly via dimerization of cyclic, four-membered intermediates (ENSN and E′NSN, Scheme 2a).[16]

The reactions between $(Me_3SiNSN)_2E$ (E = S, Se) and $TeCl_4$ seem to follow a slightly different pathway by producing nonionic, five-membered Cl_2TeESN_2 ring compounds with several byproducts, as shown in eq 1.

The reaction is probably initiated by the cleavage of one Si−N bond and the elimination of Me_3SiCl followed by the formation of an intermediate $Cl_3TeNSNENSNSiMe_3$ (Scheme 2b). Subsequent elimination of another molecule of Me_3SiCl and N_2 yields Cl_2TeESN_2 and S_4N_4. The reaction of $(Me_3SiNSN)_2S$ with $SeCl_4$ leads to the formation of $SeCl_2$ and S_4N_4 (Scheme 2c), as concluded by NMR spectroscopy.[63] It seems that the reduction of $SeCl_4$ to $SeCl_2$ is more favorable than that of $TeCl_4$ to $TeCl_2$ and could provide an

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

(54) Anderson, D. G.; Robertson, H. E.; Rankin, D. W. H.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 859.

(55) Schubert, G.; Kiel, G.; Gattow, G. *Z. Anorg. Allg. Chem.* **1989**, *575*, 129.

(56) The sum of the covalent radii for tellurium and nitrogen is 2.07 Å.[57]

(57) Emsley, J. *The Elements*, 3rd ed.; Clarendon Press: Oxford, U.K., 1998.

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

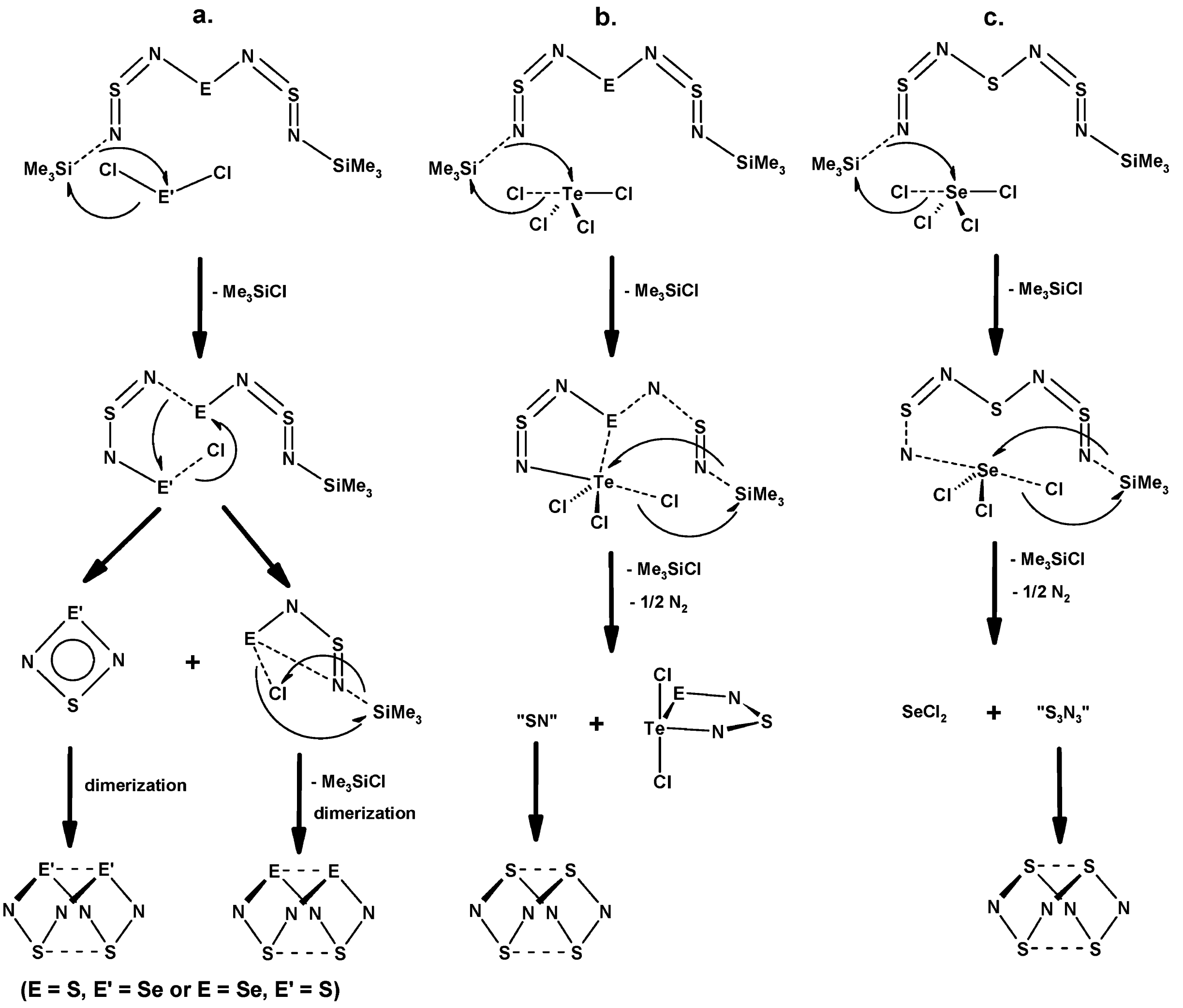
(59) Haas, A.; Pohl, R. *Chimia* **1989**, *43*, 261.

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

(61) Alcock, N. W.; Harrison, W. D. *J. Chem. Soc., Dalton Trans.* **1982**, 251.

(62) Boese, R.; Haas, A.; Hoppmann, E.; Merz, K.; Olteanu, A. *Z. Anorg. Allg. Chem.* **2002**, *628*, 673.

Scheme 2



explanation for the differing routes in reactions involving $TeCl_4$ and $SeCl_4$.

Reactions of $(Me_3SiNSN)_2Se$ with $[PPh_4]_2[Pd_2X_6]$ (X = Cl, Br). The reaction of $(Me_3SiNSN)_2Se$ with $[PPh_4]_2[Pd_2X_6]$ in CH_2Cl_2 over the course of 48 h results in solutions from which well-formed crystals of $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)X_4]$ (X = Cl **4a**, Br **4b**) may be grown via slow diethyl ether diffusion over the course of many days (eq 2).

$$2\ (Me_3SiNSN)_2Se + [PPh_4]_2[Pd_2X_6] \rightarrow [PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)X_4] + 2Me_3SiX + Me_3SiSiMe_3 + {}^3/_2N_2 + {}^3/_4S_4N_4\ (X = Cl, Br) \quad (2)$$

In both cases, the crystals are of sufficient size to make separation from amorphous byproducts relatively easy and yields of 47 (**4a**) and 58% (**4b**) are attainable in this manner.

Crystal Structures of 4a and 4b. The X-ray crystal structures of **4a** and **4b** are shown in Figure 4. The relevant bond parameters are summarized in Table 4. The anions in both cases are isostructural and effectively analogous to those in $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2S)Br_4]$.[23] In **4a** and **4b**, the two selenium atoms are in the bridging positions. The planar, five-membered Se_2N_2S ligand thus links the two PdX_2 units in **4a** and **4b** via Pd−Se bonds of average length of 2.382 and 2.391 Å, respectively, resulting in square-planar geometry around the Pd atom. The Pd−Se bond lengths are comparable to those of 2.389(1) and 2.335(1) Å observed for $[(PPh_3)_2N]_2[Cl_2Pd(\mu\text{-}SePh)_2PdCl_2]\cdot MeCN$[65] that also contains a three-coordinated, bridging selenium between two Pd-atoms. Perhaps the most noteworthy feature of both structures is the disparity of bond lengths within the Se_2N_2S ligands in **4a** and **4b**: The Se−N bond lengths are comparable to the single bond distances of 1.844(3), 1.827(5), and 1.869(2) Å observed for $(Me_3SiNSN)_2Se$,[16] $(OSN)_2Se$,[53] and $[(Me_3Si)_2N]_2Se$,[58] respectively. By contrast, the S−N distances are 1.551(4) and 1.555(4) Å in **4a** and 1.553(3) and

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(63) The reaction between $SeCl_4$ and $(Me_3SiNSN)_2S$ was conducted similarily to those of $(Me_3SiNSN)_2E$ (E = S, Se) with $TeCl_4$ (see Experimental Section). Precipitation of $Cl_2SeS_2N_2$ was not observed during or after the reaction. NMR spectra of the reaction solution (CH_2Cl_2, 25 °C, δ): ^{13}C 2.78 (Me_3SiCl); ^{14}N −256 (S_4N_4); ^{77}Se 1766 ($SeCl_2$). After a few hours, the ^{77}Se NMR spectrum also showed a resonance at δ 1279 (Se_2Cl_2) because of the disproportionation: $3\ SeCl_2 \leftrightarrow Se_2Cl_2 + SeCl_4$.[64] The resonance of $SeCl_4$ was not observed because of its low solubility in CH_2Cl_2.

(64) Maaninen, A.; Chivers, T.; Parvez, M.; Pietikäinen, J.; Laitinen; R. S. *Inorg. Chem.* **1999**, *38*, 4093.

(65) Liaw, W.-F.; Chou, S.-Y.; Jung, S.-J.; Lee, G.-H.; Peng, S.-M. *Inorg. Chim. Acta* **1999**, *286*, 155.

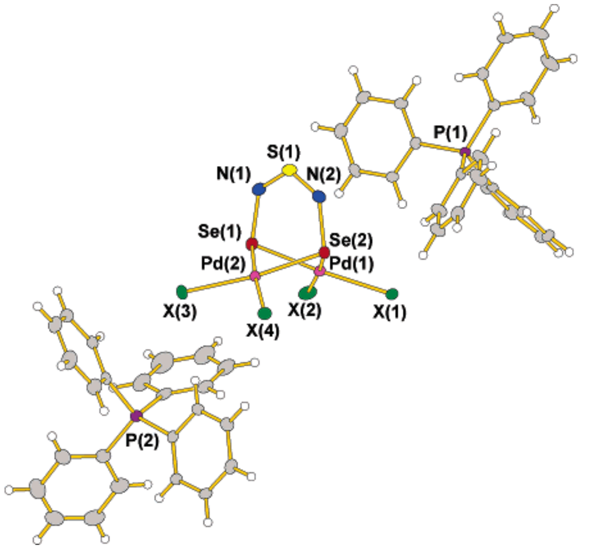
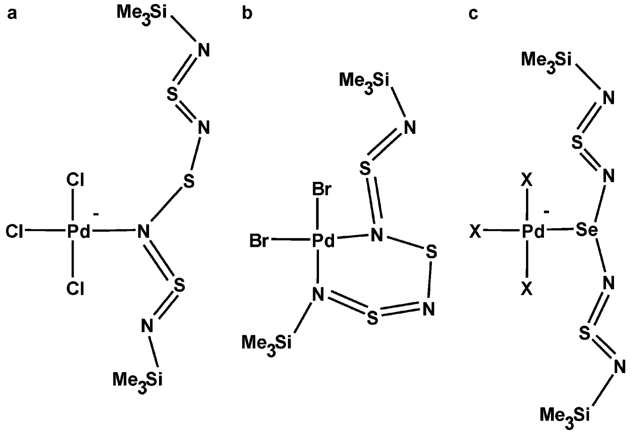


Figure 4. Crystal structures of $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)X_4]$ [X = Cl (**4a**), Br (**4b**)] indicating the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

1.556(4) Å in **4b**, which are values close to the double bond lengths of sulfur and nitrogen.[52] Thus, it would appear that multiple bonding within the ligand is localized on the N═S═N unit. In the case of $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2S)Br_4]$,[23] the delocalization of the double bond across the ligand is more pronounced with the bond lengths of 1.61(5) and 1.56(4) Å within the N═S═N unit and 1.65(3) and 1.64(5) Å for the S−N single bonds.[52] The Se atoms show a distorted tetrahedral bonding environment. This is consistent with the formal localization of the negative charge to the selenium atoms. The $[Pd_2(\mu\text{-}Se_2N_2S)X_4]^{2-}$ anions are surrounded by the large $(PPh_4)^+$ cations and, therefore, no significant intermolecular close contacts are observed in the structures of **4a** and **4b**.

Formation of $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)X_4]$ (X = Cl, Br). The anions within **4a** and **4b** are effectively analogous to those found previously in $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2S)X_4]$ (X = Cl, Br) with the two selenium atoms occupying the bridging positions.[26] Indeed, it was the ability of $(Me_3SiNSN)_2S$ to act as a source of the latter species which prompted our investigation into analogous reactions of $(Me_3SiNSN)_2Se$. However, while the aforementioned products have clear similarities, there are important contrasts between the reactions. While the reactions involving $(Me_3SiNSN)_2S$ also generate salts of other anions, namely, $[Pd(N_3S_2)Cl_2]^-$, $[Pd(N_3S_2)Br_2]^-$, and $[Pd_2(S_2N_2)Br_6]^{2-}$,[23] none of these appear to form in the reactions of $(Me_3SiNSN)_2Se$, nor are any partially selenated variations upon those systems found. This suggests that the pathways for the reactions involving $(Me_3SiNSN)_2Se$ are subtly different to those involving $(Me_3SiNSN)_2S$. In the latter case, reactions are dependent upon the nature of the halide present, and initial products of the type $[Pd\{(Me_3SiNSN)_2S\}Cl_3]^-$ (with the incoming ligand N-bound in monodentate fashion) and $[Pd\{(Me_3SiNSN)_2S\}Br_2]^-$ (with bidentate ligand) were postulated (Scheme 3a, b).[23]

Scheme 3



The presence of Pd−N bonds in both intermediates would allow for ready formation of the complexes of $[N_3S_2]^-$ and S_2N_2, and indeed the yield of the complexes of $[S_3N_2]^{2-}$ is very low in both cases (these complexes can be formed in much greater yield using S_4N_4 as starting material).[26] The relatively high yields of the Pd−Se bond-bearing anions in **4a** and **4b** suggest that a likely intermediate in both reactions is one of the type $[Pd\{(Me_3SiNSN)_2Se\}X_3]^-$ in which the ligand is bound to the metal via the softer selenium atom (Scheme 3c). We may then envisage two such units coming together to rearrange; both Me_3SiX and $Me_3SiSiMe_3$ can be detected as products when the reactions are performed in CD_2Cl_2 and monitored by ^1H NMR.

Table 4. Selected Bond Lengths (Å) and Angles (°) of $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)Cl_4]$ (**4a**) and $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)Br_4]$ (**4b**)

	4a	4b		4a	4b
Se(1)−N(1)	1.831(4)	1.829(3)	Se(2)−Pd(1)	2.3796(6)	2.3884(4)
Se(2)−N(2)	1.835(4)	1.829(3)	Se(2)−Pd(2)	2.3837(6)	2.3940(4)
S(1)−N(1)	1.551(4)	1.556(4)	Pd(1)−X(1)	2.360(1)	2.4750(5)
S(1)−N(2)	1.555(4)	1.553(3)	Pd(1)−X(2)	2.364(1)	2.4796(5)
Se(1)−Pd(1)	2.3842(6)	2.3898(5)	Pd(2)−X(3)	2.337(1)	2.4548(5)
Se(1)−Pd(2)	2.3703(6)	2.3749(5)	Pd(2)−X(4)	2.365(1)	2.4832(5)
Se(1)−N(1)−S(1)	126.3(2)	126.5(2)	Pd(1)−Se(2)−Pd(2)	82.04(2)	80.33(1)
N(1)−S(1)−N(2)	122.8(2)	122.7(2)	Se(1)−Pd(1)−X(1)	173.51(3)	173.82(2)
S(1)−N(2)−Se(2)	126.2(2)	127.0(2)	Se(1)−Pd(1)−X(2)	90.13(3)	90.07(2)
Se(1)−Pd(1)−Se(2)	84.97(2)	85.52(2)	Se(1)−Pd(2)−X(3)	87.46(3)	86.88(2)
Se(1)−Pd(2)−Se(2)	85.19(2)	85.72(2)	Se(1)−Pd(2)−X(4)	174.06(3)	174.28(2)
Pd(1)−Se(1)−N(1)	104.1(1)	103.3(1)	Se(2)−Pd(1)−X(1)	88.81(3)	88.66(2)
Pd(1)−Se(2)−N(2)	104.2(1)	105.0(1)	Se(2)−Pd(1)−X(2)	174.12(4)	173.81(2)
Pd(2)−Se(1)−N(1)	104.6(1)	105.0(1)	Se(2)−Pd(2)−X(3)	171.96(4)	171.87(2)
Pd(2)−Se(2)−N(2)	103.5(1)	103.3(1)	Se(2)−Pd(2)−X(4)	90.83(3)	90.89(2)
Pd(1)−Se(1)−Pd(2)	82.23(2)	80.69(2)			

Conclusions

While the reactions of $(Me_3SiNSN)_2E$ with $E'Cl_2$ (E = S, Se) afford eight-membered cage molecules, $EE'S_2N_4$,[16] the reactions of $(Me_3SiNSN)_2E$ with $TeCl_4$ (E = S, Se) produce five-membered rings, Cl_2TeESN_2, as the main products. The products were characterized by X-ray crystallography, NMR, and Raman and mass spectroscopy. The isolation of $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)X_4]$ confirms the potential of $(Me_3SiNSN)_2Se$ as a synthon within transition-metal chemistry. It also indicates that it is possible to introduce selenium into larger chalcogen-nitrogen ligand systems, suggesting that many more await discovery.

Acknowledgment. The financial support from the Academy of Finland, Emil Aaltonen Foundation, Finnish Cultural Foundation's Regional Fund of North Ostrobothnia, NSERC (Canada), EPSRC (UK) for provision of PDRA is gratefully acknowledged. We also thank Johnson Matthey for loans of precious metals.

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

IC050261F