Syntheses and Properties of $X_6Te_2N_2Se$ (X=Cl, Br): Stable Heterocycles with an N=Se=N Moiety

Alois Haas* and Mike Schäfers

Lehrstuhl für Anorganische Chemie II der Ruhr-Universität Bochum,
D-44780 Bochum, Germany

Received October 7, 1994

Key Words: Ditellurium(IV), di-μ-halogeno-tetrahalogeno-μ-(selenium diimidato) / Selane, bis[bis(trimethylsilyl)amido]- / Diselane, bis[bis(trimethylsilyl)amido]

Treatment of $Se[N(SiMe_3)_2]_2$ with TeX_4 (X = Cl, Br) yields new bicyclic tellura heterocycles $X_6Te_2N_2Se$ (X = Cl, **1a**; X = Br, **1b**). Similarly, these compounds are obtained with elimination of elemental selenium by reaction of $Se_2[N(SiMe_3)_2]_2$ with TeX_4 (X = Cl, Br). They are characterized by IR and mass spectroscopy as well as elemental analyses. ^{125}Te- and ^{77}Se-NMR data are given for $Cl_6Te_2N_2Se$ (**1a**), and spectra are compared with those of the corresponding sulfur analogs.

The interest in inorganic Te−N chemistry[1] has increased since the new starting materials $E(NSO)_2$ (E = Se[2], Te[3]) have become available on a preparative scale. Recently, we have reported on tellurium-containing heterocycles such as $X_6Te_2N_2S$ (X = Cl, **2a**; Br, **2b**)[4,5], $X_2\overline{TeNSNSe}$ (X = Cl, Br)[4,5], and $[F\overline{TeNSNSeNSN}]^+[TeF_5^-]$[5] prepared by treatment of $Se(NSO)_2$ with tellurium halides. Attempts to use $Te(NSO)_2$ as a precursor for the synthesis of tellura rings have been less successful.

Only the polymer $[Cl_3Sb \cdot Cl \cdot Cl\overline{TeNSNS}]_n$ has been prepared by reaction of $Te(NSO)_2$ with $SbCl_5$[3]. Another useful reaction pathway for the preparation of such ring systems involves treatment of $S[N(SiMe_3)_2]_2$ with tellurium haildes or mixtures of tellurium-containing chalcogen halides yielding $X_2\overline{TeNSNE}$ (E = S, X = Cl, Br; E = Se, X = Cl, Br, I; E = Te, X = Cl, Br)[4,6].

Recently, Chivers et al. have described analogous reactions of $Se[N(SiMe_3)_2]_2$ with selenium halides[7]; $[\overline{SeNSeNSe}Cl]Cl$ and its dimer $[\overline{SeNSeNSe}]_2Cl_2$ are obtained by treatment of $Se[N(SiMe_3)_2]_2$ with mixtures of $SeCl_4$ and Se_2Cl_2 in a Se:Cl ratio of 1:3 or 2:5, respectively.

These results have prompted us to investigate the reactions of $Se[N(SiMe_3)_2]_2$ and $Se_2[N(SiMe_3)_2]_2$ with tellurium halides to obtain tellurium-containing heterocycles with a N=Se=N function.

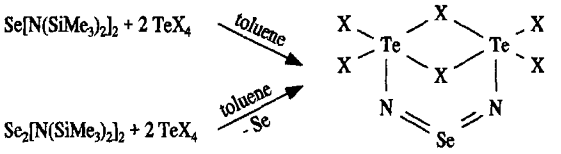
Results and Discussion

Several types of chalcogen-nitrogen ring systems with a N=S=N fragment have been prepared and structurally characterized[1].

In contrast to this, only a limited number of heterocycles with a N=Se=N function have been synthesized: $Se_3N_2Cl^+Cl^-$, $[Se_3N_2Cl_2]_2$[7], $[Se_3N_2]_2^{2+}$, $Se_3N_2^{2+}$[8], and $Se_3N_2Cl^+GaCl_4^-$[9].

We now report on the syntheses of di-μ-chloro-tetrachloro-1κ^2*Cl*,2κ^2*Cl*-μ-[selenium diimidato(2−)-1κ*N*,2κ*N*]ditellurium(IV) (**1a**) and di-μ-bromo-tetrabromo-1κ^2*Br*,1κ^2*Br*-μ-[selenium diimidato(2−)-1κ*N*,2κ*N′*]ditellurium(IV) (**1b**), the first cyclic $\overline{TeNSeNTe}$ species.

Treatment of $Se[N(SiMe_3)_2]_2$ with TeX_4 (X = Cl, Br) in toluene provides the bicyclic ring systems $Cl_6Te_2N_2Se$ (**1a**) and $Br_6Te_2N_2Se$ (**1b**) as an unexplosive red-brown powder in 82% (75%) yield according to eq. (1)[10] (data of **1b** in brackets). Attempts to prepare the analogous $F_6Te_2N_2Se$ and $I_6Te_2N_2Se$ have failed even at elevated temperatures.



(1)

1a: X = Cl

1b: X = Br

The products are insoluble in ordinary organic solvents and in liquid SO_2, whereas **1a** dissolves in a mixture of $SeOCl_2$ with benzene (1:5). This solution is stable enough to measure immediately ^{77}Se- and ^{125}Te-NMR spectra.

The red solution exhibits a ^{125}Te-NMR resonance at δ = 1612, in good agreement with its proposed bicyclic structure containing two equivalent tellurium atoms and with δ = 1739[14] for its sulfur analog **2a**.

The ^{77}Se-NMR spectrum exhibits a singlet at δ = 1290 comparable with δ(Se) in the selenium diimide complex $\{SnCl_4$-$[(BuᵗN=)_2Se]\}$, whose signal is observed at δ = 1392[11].

The IR spectra of the bicyclic systems **1a** and **1b** are similar to the few published IR data of ring systems with N=Se=N functions[7,9]. The frequencies 745 (vs) [715 (vs)] and 703 cm^{-1} (s) [677 (s)] are both assigned to the stretching modes ν_{as} and ν_s(NSeN) usually observed in the region between 900 and 700 cm^{-1}. They are lower than in 1,2,4,3,5-triselenadiazolylium rings because of mass effects. In the moiety Te−N=Se=N−Te vibrations of the two N atoms are influenced by the higher mass of Te similar to Se in the Se−N=Se=N−Se fragment. A comparison of IR and mass spectral data between **1a** and **1b** given in Tables 1 and 2 and their isostructural sulfur analogs **2a** and **2b** show the expected similarities. The IR spectra of **1a** and **1b** are identical in number, intensities, and shape of bands. The vibrations are shifted to lower wave numbers by about 22 to 33 cm^{-1} going from chlorine to bromine substituents but the overall pattern, accept additional bands at 832 cm^{-1} (m) for **1a** and 805 cm^{-1} (m) for **1b**, is similar. The origin of these additional vibration may come by combination of, e.g., ν(Te−N) and ν(Te−X) with X = Cl, Br.

0009−2940/95/0404−0437 $ 10.00+.25/0

The bands at 567 cm^{-1} (534) are attributed to ν(Te−N) modes comparable with those of **2a** at 559 cm^{-1}[4].

Table 1. Infrared spectral data [cm^{-1}] for $X_6Te_2N_2E$, [X = Cl, Br, E = S, Se]

X = Cl, E = S[5]	X = Cl, E = Se **1a**	X = Br, E = S[5]	X = Br, E = Se **1b**	Tentative Assignment
1129 (vs)		1111 (vs)		$\nu_{as}(N{=}S{=}N)$
	832 (m)		805 (m)	combination band?
	745 (vs)		715 (vs)	$\nu_{as}(N{=}Se{=}N)$
1080 (m)		1055 (m)		$\nu_s(N{=}S{=}N)$
	703 (s)		677 (s)	$\nu_s(N{=}Se{=}N)$
	613 (w)		591 (w)	
559 (m)	567 (m)	539 (w)	534 (m)	ν(Te−N)

Table 2. Mass spectral data for $X_6Te_2N_2E$ [X = Cl, Br, E = S, Se]

m/z Intensity (%)	X = Cl, E = S[4] **2a**	X = Cl, E = Se **1a**	X = Br, E = S[5] **2b**	X = Br, E = Se **1b**
288	–	–	$TeBr_2^+$ (53)	$TeBr_2^+$ (42)
235	$TeCl_3^+$ (75)	$TeCl_3^+$ (6)	–	–
209	–	–	$TeBr^+$ (100)	$TeBr^+$ (77)
200	$TeCl_2^+$ (78)	$TeCl_2^+$ (39)	–	–
165	$TeCl^+$ (100)	$TeCl^+$ (77)	–	–
160	–	–	Br_2^+ (27)	–
144	–	TeN^+ (2)	TeN^+ (4)	TeN^+ (4)
130	Te^+ (34)	Te^+ (24)	Te^+ (24)	Te^+ (40)
94	–	NSe^+ (4)	–	NSe^+ (2)
92	–	–	$N_2S_2^+$ (10)	–
81	$SNCl^+$ (15)	–	–	–
80	–	Se^+ (40)	–	Se^+ (98)
79	–	–	Br^+ (37)	Br^+ (100)
46	SN^+ (45)	–	SN^+ (32)	–
35/36	Cl^+ (35)	Cl^+ (84)	–	–
32	S^+ (6)	–	S^+ (6)	–
28	–	–	N_2^+ (4)	–

Mass spectroscopic investigations provide no M^+ peaks, but important main fragments such as TeN^+, SeN^+, and $TeX_n{}^+$ (X = Cl, *n* = 1,2,3; X = Br, *n* = 1,2) are observed in good agreement with those reported for the bicyclic system **2a**[4] and **2b**[5]. Main evidence of the given formulas is provided by complete elemental analyses of $Br_6Te_2N_2Se$ and Cl, N analyses of $Cl_6Te_2N_2Se$.

The analogous reaction of $Se_2[N(SiMe_3)_2]_2$ with TeX_4 (X = Cl, Br) yields **1a** or **1b** and elemental selenium in stoichiometric amounts as an inseparable mixture as proved by elemental analyses (see experimental section). This procedure cannot be considered a preparative method.

Reduction of the corresponding sulfur-containing bicyclic systems **2a** and **2b** with $SbPh_3$ provides the five-membered ring systems $X_2\overline{TeNSNTe}$[5,12]. These results have prompted us to study this reaction in a similar manner.

The accomplished experiments demonstrate that the dehalogenation of **1a** or **1b** with $SbPh_3$, PPh_3, or $SnCl_2$ carried out at varying temperatures provide only elemental tellurium as the sole detectable product. Moreover, treatment of **1a** or **1b** with Lewis acids to obtain soluble salts have been unsuccessful, probably due to the insolubility of these compounds.

We thank the *Ministerium für Wissenschaft und Forschung (NRW)*, the *Deutsche Forschungsgemeinschaft*, and the *Fonds der Chemischen Industrie* for financial support.

Experimental

All reactions were carried out by using a vacuum line or in a glove box (Co. M. Braun GmbH, München) under argon dried with Sicapent. All solvents (except $SeOCl_2$) were dried according to published procedures[13] and transferred from activated molecular sieves (4 Å). – Elemental analyses: Microanalytical Laboratory of our institute or Microanalytical Laboratory Pascher, Remagen. – IR: KBr discs, Bruker FT-IR IFS 85 (4000–400 cm^{-1}). – MS: Varian MAT CH7 (70 eV, emission 100 μA). – NMR: WM 250 PFT (S. 87 T), standards Me_2Se(^{77}Se), Me_2Te(^{125}Te). – $[(Me_3Si)_2N]_2Se$ and $[(Me_3Si)_2N]_2Se_2$ were prepared by published methods[2]. Commercially available $TeCl_4$ and $TeBr_4$ were not further purified.

Di-μ-chloro-tetrachloro-1κ²Cl,2κ²Cl-[μ-selenium diimidato(2−)-1κN,2κN']ditellurium(IV) (**1a**): A glass apparatus consisting of two 50-ml Carius tubes with Teflon valves and a medium-sintered glass frit was used for the synthesis. One tube contained a suspension of 1.08 g (4.0 mmol) of $TeCl_4$ in 20 ml of toluene and the other a solution of 0.9 g (2.3 mmol) of $Se[N(SiMe_3)_2]_2$ in toluene, which was added in small portions to the $TeCl_4$ suspension at 20°C. This reaction mixture was stirred for 1 d, and formation of a red-brown solid was observed., Formation of $(CH_3)_3SiCl$ was confirmed by its IR spectrum in the gas phase. After 3 d the yellow solution was separated by filtration, and the remaining solid was washed several times with toluene. After removal of the volatile materials the solid was dried in vacuo for 24 h. The red-brown precipitate was insoluble in organic solvents and SO_2, but readily soluble in $SeOCl_2$/benzene (1:5), although rapid decomposition was observed. After NMR measurements (not more than 1 h) it was possible to recover **1a** by evaporating the solution to dryness. During this procedure **1a** is deposited as a powder, sticked at the walls (characterized by an IR spectrum) and an oil at the bottom of the NMR tube. In the presence of moist air decomposition took place. Yield 0.95 g (≈ 82%), m.p. > 200°C. – ^{77}Se NMR ($SeOCl_2/C_6D_6$): δ = 1290. – ^{125}Te NMR ($SeOCl_2/C_6D_6$): δ = 1612. – IR: ṽ = 832 cm^{-1} (m), 745 (vs), 703 (s), 613 (w), 567 (m). – MS, *m/z* (%): 235 (6) [Cl_3Te^+], 200 (39) [Cl_2Te^+], 165 (77) [$ClTe^+$], 144 (2) [NTe^+], 130 (24) [Te^+], 94 (4) [NSe^+], 80 (40) [Se^+], 36 (84) [Cl^+]. – $Cl_6N_2SeTe_2$ (572.2): calcd. Cl 37.0, N 4.9; found Cl 36.1, N 4.7.

Reaction of $Se_2[N(SiMe_3)_2]_2$ with $TeCl_4$: In an analogous procedure 1.0 g (3.7 mmol) of $TeCl_4$ and 0.9 g (1.9 mmol) of $Se_2[N(SiMe_3)_2]_2$ yielded 1.0 g of a red-brown inseparable mixture of **1a** and elemental selenium. IR and mass spectra were identical with **1a**. – $Cl_6N_2SeTe_2$ + Se (1:1): calcd. Cl 32.7, N 4.3; found Cl 32.0, N 4.0.

Di-μ-bromo-tetrabromo-1κ²Br,2κ²Br-μ-[selenium diimidato(2−)-1κN,2κN']ditellurium(IV) (**1b**): According to the method described above one tube was filled with a suspension of 1.6 g (3.5 mmol) of $TeBr_4$ in 20 ml of toluene and the other tube with a solution of 0.87 g (2.2 mmol) of $Se[N(SiMe_3)_2]_2$ in 10 ml of toluene. The latter was added in small portions to the $TeBr_4$ suspension at 20°C, and the reaction mixture was stirred for 1 d. Formation of a brown precipitate was observed. The mixture was stirred for additional 2 d and the brown suspension separated by filtration. The remaining solid was washed several times with toluene and dried in vacuo for 24 h. It was insoluble in organic solvents and SO_2. In $SeOCl_2$ it decomposed very rapidly. The brown solid hydrolyzed in the presence of moist air. Yield 2.13 g (75%), m.p. > 200°C. – IR: ṽ = 805 cm^{-1} (m), 715 (vs), 677 (vs), 591 (w), 534 (m). – MS, *m/z* (%): 288 (42) [Br_2Te^+], 209 (77) [$BrTe^+$], 144 (4) [NTe^+], 130 (40) [Te^+], 94 (2) [NSe^+], 80 (98) [Se^+], 79 (100) [Br^+]. – $Br_6N_2SeTe_2$

(813.6): calcd. Br 57.0, N 3.4, Se 9.4, Te 30.3; found Br 56.0, N 3.0, Se 10.0, Te 29.7.

Reaction of $Se_2[N(SiMe_3)_2]_2$ with $TeBr_4$: In an analogous procedure 1.2 g (2.6 mmol) of $TeBr_4$ and 0.64 g (1.3 mmol) of $Se_2[N(SiMe_3)_2]_2$ yielded 0.95 g of a red-brown inseparable mixture of **1b** and elemental selenium. IR and mass spectra were identical with those of **1b**.

---

[1] A. Haas, J. Kasprowski, M. Pryka, *Coord. Chem. Rev.* **1994**, *130*, 301–353.

[2] A. Haas, J. Kasprowski, K. Angermund, P. Betz, C. Krüger, Y.-H. Tsay, S. Werner, *Chem. Ber.* **1991**, *124*, 1985–1906.

[3] A. Haas, R. Pohl, *Chimia* **1989**, *43*, 261–262; *Eur. J. Solid. State Inorg. Chem.* **1992**, *29*, 791; R. Boese, J. Dworak, A. Haas, M. Pryka, *Chem. Ber.*, in press.

[4] A. Haas, J. Kasprowski, M. Pryka, *Chem. Ber.* **1992**, *125*, 1537–1540.

[5] A. Haas, M. Pryka, *Chem. Ber.* **1995**, *128*, 11–22.

[6] A. Haas, M. Pryka, M. Schäfers, *Chem. Ber.* **1994**, *127*, 1865–1870.

[7] J. Siivari, T. Chivers, R. Laitinen, *Angew. Chem.* **1992**, *104*, 1539–1540; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1518; J. Siivari, T. Chivers, R. Laitinen, *Inorg. Chem.* **1993**, *32*, 4391–4395.

[8] E. G. Awere, J. Passmore, P. S. White, T. Klapötke, *J. Chem. Soc., Chem. Commun.* **1989**, 1415–1417.

[9] R. Wollert, B. Neumüller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1992**, *616*, 191–194.

[10] The same reaction performed in CH_2Cl_2 yields a green-grey solid with the composition $CCl_6H_2N_2SeTe_2$ (proved by complete elemental analysis). IR- and mass spectroscopic data were analogous with those of **1a**.

[11] I. Gindl, M. Björgvinsson, H. W. Roesky, C. Freire-Erdbrügger, G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, **1993**, 811–812.

[12] A. Haas, J. Kasprowski, M. Pryka, *J. Chem. Soc., Chem. Commun.* **1992**, *16*, 1144–1145.

[13] *Methoden Org. Chem. (Houben-Weyl)* (Ed.: E. Müller), Thieme, Stuttgart, **1959**, vol. I/2, p. 765; *Organikum*, 15th ed., VEB Deutscher Verlag der Wissenschaften, Berlin **1977**, p. 231.

[14] M. Pryka, Dissertation, Universität Bochum, **1993**.

[385/94]