Synthesis and Characterization of $Cl_2\overline{TeNSNTe}$ and $[Cl\overline{TeNSNTe}][AsF_6]$

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The first five-membered chalcogen–nitrogen ring system, containing two Te atoms, $Cl_2\overline{TeNSNTe}$, has been prepared either by dechlorination of $Cl_6Te_2N_2S$ with Ph_3Sb or by reaction of $S[N(SiMe_3)_2]_2$ with $TeCl_4$; treatment of $Cl_2\overline{TeNSNTe}$ with AsF_5 in liquid SO_2 leads to the formation of $[Cl\overline{TeNSNTe}]^+[AsF_6]^-$, and the molecular structure of this salt has been determined by X-ray crystallography.

During the past few years several types of compounds with cyclic and cage SeSN moieties[1,2] as well as the first examples of binary SeN cations[3] have been prepared and structurally characterized. These developments have resulted in increased interest in analogous TeN compounds. So far only a limited number of TeN species have been synthesized: $Te(NSO)_2$,[4] $Te[N(SiMe_3)_2]_2$,[5] $\overline{SNSNTe}Cl{\cdot}Cl{\cdot}SbCl_3$,[6] $(ClTeNSN)_3N$,[7] $Cl_6Te_2N_2S$[8] and $Cl_2\overline{TeNSNSe}$.[9]

We report here the synthesis of 3,3-dichloro-1,3λ^4,4,2,5-thiaditelluradiazole **1** and 3-chloro-1,3,4,2,5-thiaditelluradiazolium hexafluoroarsenate **2**, the first cyclic $\overline{TeNSNTe}$ species.

Compound **1** was obtained by the addition of a solution of Ph_3Sb (9.4 mmol) in CH_2Cl_2 (10 ml) to a suspension of $Cl_6Te_2N_2S$ (4.7 mmol) in CH_2Cl_2 (10 ml) (Scheme 1). The precipitate formed was filtered off with exclusion of moisture and washed several times with CH_2Cl_2. A dark-red crystalline powder was obtained in yields of >95%. The air-sensitive product is insoluble in CH_2Cl_2 or SO_2, does not explode on mechanical shock or heating and melts at 250 °C (decomp.). The results of a vibrational spectroscopic study† are in good agreement with the proposed five-membered ring structure and correspond well with spectra of the selenium analogue $Cl_2\overline{SeNSNSe}$[1] and $Cl_2\overline{TeNSNSe}$.[9]

The product of the reaction of $TeCl_4$ with $S[N(SiMe_3)_2]_2$ in CH_2Cl_2 in a 1 : 1 molar ratio is a red-brown powder, which contains **1** as the main component (80–90%). So far the impurities present (containing Me_3Si ligands) could not be separated or identified.

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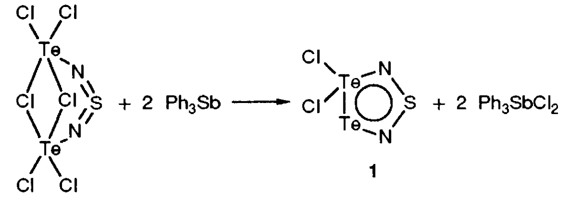
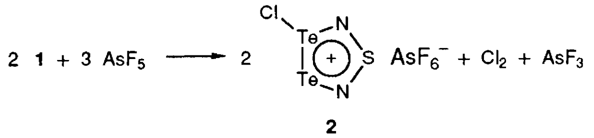
† *Spectroscopic data* for **1**: IR (KBr) ν/cm^{-1}: 1037vs, 936vs, 587s, 519s. Raman shifts (sealed glass capillaries) ν/cm^{-1}: 1050w, 941m, 588w, 523w, 394s, 339m, 306vs, 213m, 187vs. Mass spectrum (120 °C, main fragments): $TeCl_2^+$, $TeSN^+$, $TeCl^+$, Te^+, $S_2N_2^+$, SN^+, Cl^+, S^+. Elemental analyses for Cl, N and S are in good agreement with calculated data.



Scheme 1



Scheme 2

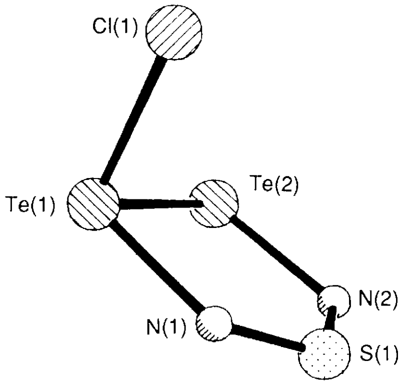


Fig. 1 The structure of the cation $\mathrm{Cl\overline{TeNSNTe}}^+$ in **2**. Bond distances (Å) and angles (°): Te(1)–Te(2) 2.731(2), Te(1)–N(1) 2.001(14), S(1)–N(2) 1.535(13), Te(1)–Cl(1) 2.336(4), Te(2)–N(2) 2.020(12), S(1)–N(1) 1.536(13); Te(2)–Te(1)–Cl(1) 101.1(1), Cl(1)–Te(1)–N(1) 97.1(4), Te(2)–N(2)–S(1) 120.6(6), Te(2)–Te(1)–N(1) 88.7(4), Te(1)–Te(2)–N(2) 88.9(3), N(2)–S(1)–N(1) 119.7(7), Te(1)–N(1)–S(1) 121.6(8).

In order to preserve the $\mathrm{\overline{TeNSNTe}}$ ring and to convert **1** into a soluble derivative the reaction with AsF_5 was studied. Using a 3 : 2 molar ratio of AsF_5 according to Scheme 2, the salt **2** was formed. In a typical experiment AsF_5 (2.6 mmol) was condensed on to a suspension of **1** (1.7 mmol) in liquid SO_2 (20 ml). The mixture was stirred for 24 h at 22 °C, resulting in a red solution. After removal of the volatile products and recrystallisation of the solid residue from liquid SO_2, compound **2** could be obtained in high yields (*ca.* 80%) as extremely air-sensitive orange-red crystals. It showed no tendency to explode on grinding or on heating during a melting point determination [m.p. 178 °C (decomp.)]. The solubility of **2** in liquid SO_2 allowed additional characterization by ^{125}Te NMR spectroscopy.‡

Single crystals were obtained from SO_2 solution by the slow removal of solvent. An X-ray crystal structure determination§ confirmed the presence of the cationic five-membered ring species as illustrated in Fig. 1. The structure shows a short Te–Te (2.731 Å) and two short Te–N single bond distances (2.001 and 2.020 Å) as expected for a delocalized, cationic ring system. The AsF_6^- anion has approximately octahedral symmetry. The cation–anion interactions are negligible.

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References

1 A. Haas, J. Kasprowski, K. Angermund, P. Betz, C. Krüger, Y.-H. Tsay and S. Werner, *Chem. Ber.*, 1991, **124**, 1895.
2 E. G. Awere, J. Passmore, P. S. White and T. Klapötke, *J. Chem. Soc., Chem. Commun.*, 1989, 1415.
3 E. G. Awere, J. Passmore and P. S. White, *Inorg. Chem.*, in the press.
4 A. Haas and R. Pohl, *Chimia*, 1989, **43**, 261.
5 M. Björgvinsson, H. W. Roesky, F. Pauer, D. Stahlke and G. M. Sheldrick, *Inorg. Chem.*, 1990, **29**, 5140.
6 A. Haas and R. Pohl, *Eur. J. Solid State Inorg. Chem.*, in the press.
7 H. W. Roesky, J. Münzenberg and M. Noltemeyer, *Angew. Chem.*, 1990, **102**, 73; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 61.
8 A. Haas, J. Kasprowski and M. Pryka, *Chem. Ber.*, 1992, **125**, 1537.
9 A. Haas, J. Kasprowski and M. Pryka, *Chem. Ber.*, 1992, **125**, 789.

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‡ *Spectroscopic data* for **2**: ^{125}Te NMR (250 MHz, C_6D_6–SO_2): δ 2304 (s) and 2241 (s) referenced to Me_2Te. The two resonances are in good agreement with the presence of cationic ring $\mathrm{Cl\overline{TeNSNTe}}^+$. IR (KBr) ν/cm^{-1}: 1050s, 949s, 699vs, 674s, 585m, 546m. Raman (sealed glass capillaries) ν/cm^{-1}: 1049w, 947m, 674m, 585m, 425s, 395w, 368m, 322vs, 234m, 214vs, 185s. Mass spectrum (180 °C, main fragments): $TeCl_2^+$, $TeClF^+$, $TeCl^+$, AsF_3^+, Te^+, AsF_2^+, SN^+. Satisfactory elemental analysis were obtained.

§ *Crystal data*: $AsClF_6N_2STe_2$, M_r = 539.7, monoclinic, space group $P2_1/n$, T = 293 K, a = 8.187(2), b = 11.756 (2), c = 10.512(2) Å, β = 90.01(3)°, V = 1011.7(4) Å^3, Z = 4, D_c = 3.543 g cm^{-3}, Mo-Kα radiation (graphite monochromator), λ = 0.71073 Å, μ = 9.53 mm^{-1}.

Empirial absorption corrections were applied to the 2329 unique reflections; of these, 1545 having $F_o \geqslant 6\sigma(F)$ were retained for structure refinements. All calculations were carried out with the SHELXTL-PLUS programs. Anisotropic thermal parameters were applied to all atoms. R = 0.059 (R_w = 0.065). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.