Synthesis and Characterisation of Tellurium-containing Chalcogen–Nitrogen Heterocycles

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$Cl_6Te_2N_2S$ and $Cl_2Br_4Te_2N_2S$ are prepared by oxidation of $Cl_2\overline{TeNSNTe}$ with Cl_2 or Br_2, respectively; reduction of $Cl_2Br_4Te_2N_2S$ with Ph_3Sb gives $Br_2\overline{TeNSNTe}$, which on treatment with $AgAsF_6$ in liquid SO_2 forms $[Br\overline{TeNSNTe}]^+[AsF_6]^-$; bromination of $Br_2\overline{TeNSNTe}$ yields the corresponding $Br_6Te_2N_2S$; attempts to prepare a dicationic five-membered ring system starting from $Cl_2\overline{TeNSNTe}$ gives the first Te containing dicationic eight-membered chalcogen–nitrogen system $[\overline{TeNSNTeNSN}]^{2+}[AsF_6^-]_2$; reaction of $Cl_6Te_2N_2S$ with $Me_3SiN{=}S{=}NSiMe_3$ leads to $Cl_4Te_2S_2N_4$.

Recent investigations of the chemical behaviour of $Se(NSO)_2$ towards tellurium containing Lewis acids such as TeX_4 (X = F, Cl) or TeX_3^+ (X = Cl) have proved $Se(NSO)_2$ to be a suitable precursor for the synthesis of tellurium-containing chalcogen-nitrogen systems.[1–3] Such compounds display novel cyclic structures possessing no analogues in sulfur–nitrogen chemistry.[2,3] High-yield synthesis of $Cl_6Te_2N_2S$[2] allows access to further interesting compounds such as $Cl_2\overline{TeNSNTe}$ and $[Cl\overline{TeNSNTe}]^+[AsF_6]^-$, which contain π-delocalisation.[4]

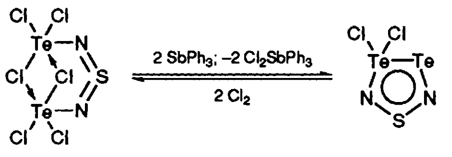
We report reactions of bicyclic $Cl_6Te_2N_2S$ and $Cl_2\overline{TeNSNTe}$, respectively, leading either to tellurium-containing chalcogen–nitrogen ring-systems or to new $Cl_6Te_2N_2S$-related compounds.

Whereas reduction of $Cl_6Te_2N_2S$ with $SbPh_3$ yields $Cl_2\overline{TeNSNTe}$,[4] chlorination with Cl_2 in CH_2Cl_2 provides $Cl_6Te_2N_2S$ again in quantitative yield (Scheme 1). Oxidation of $Cl_2\overline{TeNSNTe}$ with Br_2 (2 equiv.) is also performed successfully yielding di-μ-chloro-tetrabromo-1κ2*Br*,2κ2*Br*-μ-sulfurdiimidato (2−)-1κ*N*,2κ*N*′-ditellurium(IV) **1** (Scheme 2).

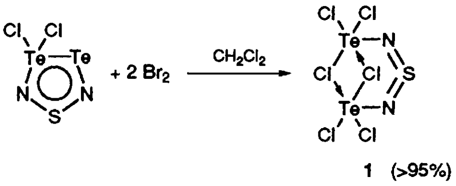
The vibrational spectra of **1** are in good agreement with those for $Cl_6Te_2N_2S$.[2] It seemed reasonable to assume C_{2v}-symmetry for **1**. Thus the two chlorine atoms must take the bridging positions as shown in Scheme 2. Compound **1** represents a high-melting yellow powder (195 °C decomp.), which is insoluble in CH_2Cl_2 and toluene.

Its reduction with $SbPh_3$ (2 equiv.) in CH_2Cl_2 selectively gives 3,3-dibromo-1,$3\lambda^4$,4,2,5-thiaditelluradiazole **2** an air-sensitive brown powder, which is insoluble in CH_2Cl_2 and in SO_2 and does not explode on mechanical shock or heating [mp 187 °C (decomp.)] (Scheme 3). The vibrational spectra of **2** correspond very well with those of $Cl_2\overline{TeNSNTe}$[4] and $Cl_2\overline{TeNSNSe}$.[1]

On treatment with $AgAsF_6$ in SO_2 **2** can be converted to the soluble, dark-red, crystalline 3-bromo-1,3,4,2,5-thiaditelluradiazolium hexafluoroarsenate **3** (Scheme 4). It showed no tendency to explode on grinding or on heating during melting [mp 192 °C (decomp.)]. The IR and Raman spectra are comparable with those of $[Cl\overline{TeNSNTe}]^+[AsF_6]^-$.[4]



Scheme 1



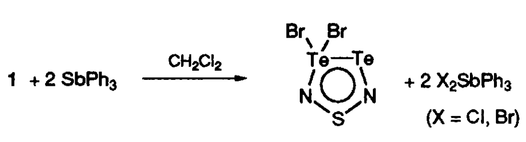
1 (>95%)

Scheme 2

When **2** is oxidised with Br_2 (2 equiv.) in CH_2Cl_2, the perbrominated derivative di-μ-bromo-tetrabromo-1κ2*Br*,2κ2*Br*-μ-sulfurdiimidato(2−)-1κ*N*,2κ*N*′ditellurium(IV) **4** is obtained (Scheme 5). Like **1**, compound **4** has vibration spectra very similar to that of $Cl_6Te_2N_2S$,[2] it is a yellow powder insoluble in common solvents [mp 180 °C (decomp.)].

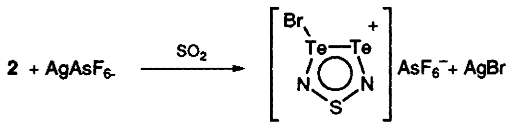
Attempts to prepare a tellurium-containing dicationic five-membered ring species $[\overline{TeNSNTe}]^{2+}$,[5–8] resulted in the novel cage like $1\lambda^4\delta^2,5\lambda^4\delta^2,3\lambda^3,7\lambda^3$,2,4,6,8-dithiaditelluratetrazocinium bis(hexafluoroarsenate) **5**. It is obtained as a yellow, crystalline product by reaction of $Cl_2\overline{TeNSNTe}$ with excess AsF_5 in SO_2 (Scheme 6). Vibrational spectroscopic bands are tentatively assigned to N=S=N stretching modes (1099m, 1059w, 1038m, and 990w cm^{-1}). The solubility in SO_2 allowed additional characterisation by ^{125}Te NMR spectroscopy.

A single crystal of **5** was examined by X-ray crystallography and despite the moderate nature of the data its structure could be elucidated as an eight-membered ring with a Te–Te cross-ring bond. The three coordinate tellurium atoms, which probably carry most of the positive charge display a pyramidal environment as illustrated in Fig. 1.† The structure shows no secondary S–S bonding and so represents a partially opened



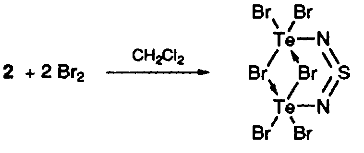
2 (>95%)

Scheme 3



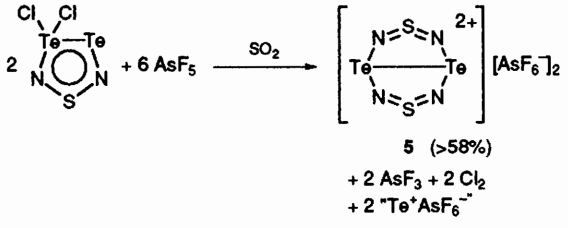
3 (>80%)

Scheme 4



4 (>95%)

Scheme 5



Scheme 6

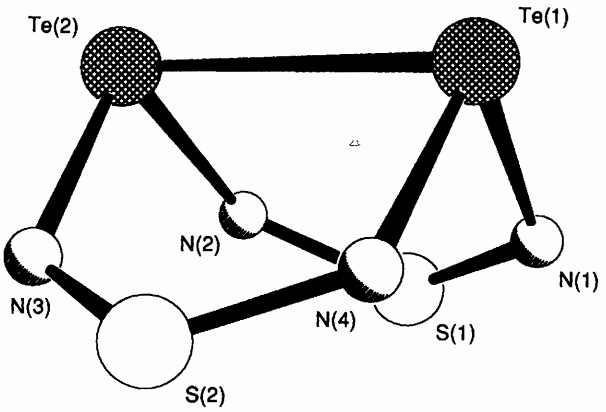


Fig. 1 The structure of the dication $Te_2S_2N_4^{2+}$ in **5**. Bond distances (Å) and angles (°): Te(1)–Te(2) 2.881(4), Te(1)–N(1) 2.044(32), Te(1)–N(4) 2.045(33), Te(2)–N(2) 2.036(31), Te(2)–N(3) 1.956(30), S(1)–N(1) 1.507(21), S(1)–N(2) 1.508(26), S(2)–N(3) 1.506(26), S(2)–N(4) 1.509(28); Te(2)–Te(1)–N(1) 87.4(7), Te(2)–Te(1)–N(4) 87.5(6), N(1)–Te(1)–N(4) 96.6(14), Te(1)–Te(2)–N(2) 85.2(6), Te(1)–Te(2)–N(3) 85.3(7), N(2)–Te(2)–N(3) 97.5(13), N(1)–S(1)–N(2) 121.2(21), N(3)–S(2)–N(4) 122.0(20), Te(1)–N(1)–S(1) 121.4(20), Te(2)–N(2)–S(1) 123.7(17), Te(2)–N(3)–S(2) 125.5(17), Te(1)–N(4)–S(2) 119.3(17).

three-dimensional cage *cf.* unsaturated $P^{V}_{2}N_4S_2$-ring systems.[9,10]

The structure of $Cl_4Te_2S_2N_4$ **6**, a product obtained by reaction of $Cl_6Te_2N_2S$ with $Me_3SiN{=}S{=}NSiMe_3$ in CH_2Cl_2 is not entirely clear. The vibration spectrum is comparable with that of $(\overline{FTeNSNSeNSN})^+[TeF_5]^-$[3] and the results of a ^{125}Te NMR spectroscopic investigation are in good agreement with an eight-membered ring having two slightly different orientated tellurium atoms.

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Footnote

† *Crystal data* for: $As_2F_{12}N_4S_2Te_2$. Yellow prism, 0.45 × 0.50 × 0.42 mm, monoclinic, space group $P2_1/c$, $a = 14.153(3)$, $b = 8.210(2)$, $c = 13.666(3)$ Å, $\beta = 111.96(3)°$, $U = 1472.7(6)$ Å^3, $Z = 4$, $M = 753.2$, $D_c = 3.397$ g cm^{-3}, absorption coefficient = 8.823 mm^{-1}, $F(000) = 1352$. Solution and refinement: Siemens SHELXTL PLUS (VMS), direct methods solution, full-matrix least-squares refinement, $\Sigma w(F_o - F_c)^2$, hydrogen atoms riding model, fixed isotropic U, $w^{-1} = \sigma^2(F) + 0.0001F^2$, disordered hexafluoroarsenate, S=N distances fixed (1.51 Å), 119 parameters refined, final R indices (obs. data) $R = 8.75\%$, $wR = 8.98\%$, goodness-of-fit 2.75. Data collection: Siemens P4 diffractometer, Mo-Kα ($\lambda = 0.71073$ Å), 293 K, highly orientated graphite crystal monochromator, $2\theta = 3.0$ to $45.0°$, ω scan-type, scan-range (ω) = 2.0°, $-15 \leq h \leq 14$, $0 \leq k \leq 8$, $0 \leq l \leq 14$, 1922 reflections collected, 1903 independent reflections, 888 [$F > 6.0\sigma(F)$] observed reflections, semiempirical absorption correction. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Fachinformationszentrum Karlsruhe. See Information for Authors, Issue No. 1.

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