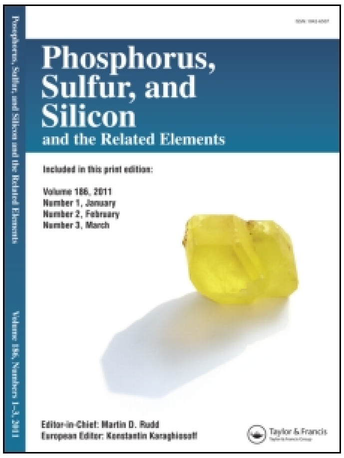

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Chalcogen-Nitrogen Compounds of the Heavier Group 16 Elements

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CHALCOGEN-NITROGEN COMPOUNDS OF THE HEAVIER GROUP 16 ELEMENTS

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Abstract Recent results of Se-N and Te-N chemistry at Göttingen University are summarized. This includes the preparation and structural characterisation of compounds with short Se-N and Te-N bonds, the first stable Te nitride, the first Te(III) radical and the first compound containing a nitrene group.

INTRODUCTION

Sulfur-nitrogen chemistry has been a well developed field of research since the 1960's. Mainly due to the greater instability of chalcogen-nitrogen bonds of the heavier elements Se and Te, not much work in this area of research has been reported until the 1980's. In this report we want to survey the results of our work. Most compounds mentioned have been investigated by X-ray analyses.

I. REACTIONS OF Se, Te HALIDES WITH N-SILYLATED IMINOPHOSPHORANES

N-Silylated iminophosphoranes have been shown to be versatile precursors to generate metal-nitrogen bonds. We were able to synthesize both cyclic[1,2] as well as acyclic[3,4,5] Se and Te iminophosphoranates.

Reactions of iminophosphorane **1** with different chalcogen halides lead to mono- or disubstituted products (equations (1) - (3)).

$$\underset{}{ChCl_4} + \underset{\mathbf{1}}{Ph_3PNSiMe_3} \longrightarrow \tfrac{1}{2}\,(Ph_3PNChCl_3)_2 \quad (1)$$

Ch = Se **2**, Ch = Te **3**.

$$ChCl_4 + 2\ \underset{\mathbf{1}}{Ph_3PNSiMe_3} \longrightarrow (Ph_3PN)_2ChCl_2 \quad (2)$$

Ch = Se **4**, Ch = Te **5**.

$$\underset{Ar\,=\,p\text{-}MeOC_6H_4}{ArTeCl_3} + \underset{\mathbf{1}}{Ph_3PNSiMe_3} \longrightarrow \underset{\mathbf{6}}{Ph_3PNTe(Ar)Cl_2} \quad (3)$$

The Ch-N bonds of all compounds exhibit partial double bond character. Compounds **5** and **6** contain the shortest Te-N bonds (191.8 pm) reported so far. While compounds **4**, **5** and **6** exist as monomers, the monosubstituted species **2** and **3** are dimeric. Dimerisation of the Se analogue **2** is achieved by Cl bridges whereas the Te compound **3** has a planar Te_2N_2 ring structure (Figure 1).

II. REACTIONS OF Se, Te HALIDES WITH N-SILYLATED N-S LIGANDS

Due to the possible explosive nature of the resulting products not many reactions of S-N ligands with Se and Te halides have been reported. We were able to stabilise Se(II)-N-S compounds with the bulky tris(trifluormethyl)phenyl ligand. Compounds **7** and **8** are nonexplosive stable molecules (equations (4), (5))[6].

$R_fSeCl + OSNSiMe_3 \longrightarrow R_fSeNSO$ (4)

$R_f = 2,4,6\text{-}(CF_3)_3C_6H_2$ **7**

$2\ R_fSeCl + S(NSiMe_3)_2 \longrightarrow S(NSeR_f)_2$ (5)

$R_f = 2,4,6\text{-}(CF_3)_3C_6H_2$ **8**

From a reaction of $TeCl_4$ with $(Me_3SiN)_2S$ we obtained the first Te nitride stable at room temperature **7** (equation (4))[7].

$TeCl_4 + S(NSiMe_3)_2 \longrightarrow (ClTeNSN)_3N$ (6)

9

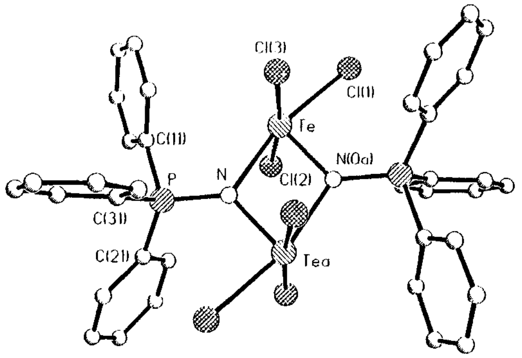

FIGURE 1 Molecular structure of **3**.

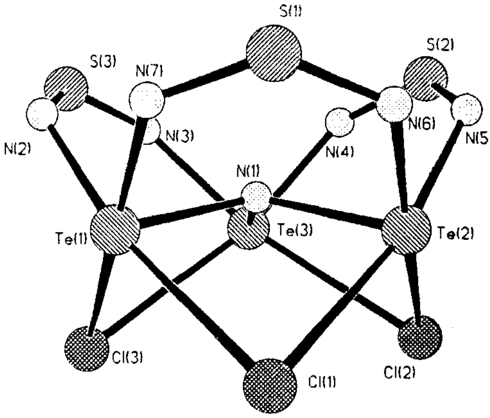

FIGURE 2 Molecular structure of **9**.

The X-ray structure analysis (Figure 2) shows a Te_3N core for **9**. The Te atoms are bridged by NSN groups and Cl atoms. The mechanism of the formation of **9** cannot fully be understood.

III. REACTION OF Se, Te HALIDES WITH Li AMIDES

In an attempt to prepare novel Se diimides $SeOCl_2$ was reacted with the Li amide **10**. From this reaction two different compounds have been isolated and structurally characterised (equation (7))[8].

$SeOCl_2 + LiN(R)SiMe_3 \longrightarrow (RN)_2Se_6 + (RN)_6Se_9$ (7)
R = tert.Bu **10** **11** **12**

Compound **11** exhibits a Se_8 crown like structure where two Se atoms have been replaced by N-tert.Bu groups. The molecular structure of **12** is shown in Figure 3.

A different reaction is observed when Se_2Cl_2 or $TeCl_4$ have been added to a solution containing an excess of Li amide (equations (8), (9))[9,10].

$Se_2Cl_2 + 2\ LiN(R)SiMe_3 \longrightarrow Se(N(R)SiMe_3)_2$ (8)
R = tert.Bu **13**, R = $SiMe_3$ **14**
$TeCl_4 + 4\ LiN(R)SiMe_3 \longrightarrow Te(N(R)SiMe_3)_2$ (9)
R = tert.Bu **15**, R = $SiMe_3$ **16**

All compounds have a V-type shape. In the structure of the Te compounds **15** and **16** weak Te-Te contacts are observed. The tert.Bu groups in **13** and **15** prefer a trans configuration.

The facile synthesis of compounds **13** - **16** makes them potential precursors for further reactions. By reacting **16** with $AgAsF_6$ the first Te(III) radical cation **17** was obtained (equation (10))[11].

16 + $AgAsF_6 \longrightarrow [Te(N(SiMe_3)_2)_2]^+AsF_6^-$ (10)
17

The radical character of this product was confirmed by a broad signal for the Me_3Si groups in the ^1H-nmr spectrum ($\Delta\nu_{\frac{1}{2}}$= 18 Hz) and the esr spectrum (g= 2,0; $\Delta\omega_{\frac{1}{2}}$= 15 G). The X-ray structure analysis showed two stabilising contacts to F atoms of the AsF_6^- counterion, thus forming chains of alternating cations and anions. Esr and X-ray structural data make it evident, that the radical electron occupies a p orbital and the lone pair a sp^2 orbital.

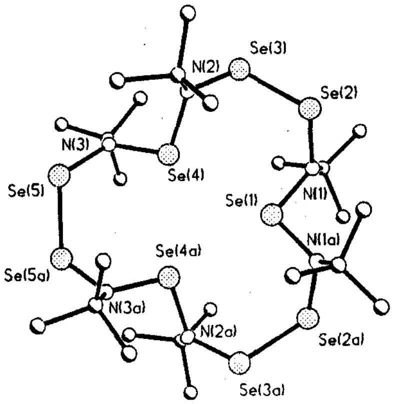

FIGURE 3 Molecular structure of **12**.

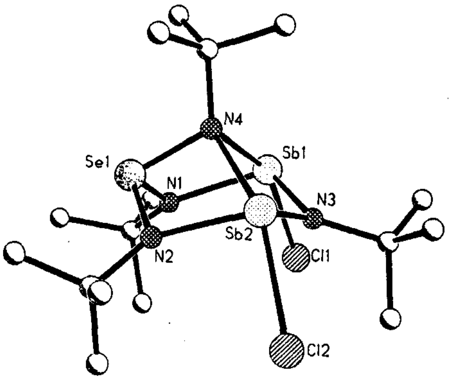

FIGURE 4 Molecular structure of **18**.

The reaction of the Se compound **13** with $SbCl_3$ leads to compound **18** containing a stabilised nitrene group (equation (11))[12].

$$\mathbf{13} + SbCl_3 \longrightarrow Se(NR)_3(SbCl)_2 \qquad (11)$$

R = tert.Bu **18**

The result of the X-ray structure analysis is shown in Figure 4. Bond distances and angles are compatible with the assumption of a high mesomeric stabilisation of the molecule.

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