Tellurium– and selenium–nitrogen compounds: preparation, characterization and properties

Alois Haas, Jörg Kasprowski and Michael Pryka

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

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Correspondence to: A. Haas, Lehrstuhl für Anorganische Chemie II der Ruhr-Universität Bochum, D-44780 Bochum, Germany.

ABSTRACT

The results of recent developments in tellurium– and selenium–nitrogen chemistry are presented with emphasis on the preparation, characterization and properties. Wherever possible, the chemistry of cyclic compounds is separated from acyclic species, which are classified according to their oxidation state. Besides conventional methods, e.g. the metathetical reaction between TeX_4 (X = F, Cl) or SeX_4 (X = Cl) and silylamines such as $[R_3Si]_nNR_{3-n}$ or $R_3SiN=S=NSiR_3$ etc., two synthons $X(NSO)_2$ (X = Se, Te) that play an important role in Se–N, Te–N and S–N heterocyclic chemistry are described here. For a better understanding, possible reaction pathways for synthesis with $Te(NSO)_2$ or $Se(NSO)_2$ are discussed and evidence for these mechanisms is provided. Attention is also paid to compounds with Se=N double bonds. Carbon-, phosphorus- and metal-containing Se–N as well as Te–N heterocycles are dealt with rather restrictively. Vibrational, mass spectroscopic and NMR data are given for important molecules.

A. INTRODUCTION

The field of Te–N and Se–N chemistry has attracted much attention in recent years, and three reviews [1–3] have been published while this article was in preparation. Here we describe the synthesis, physical properties, spectroscopic and structural data, and some chemical behaviour of Te-N and Se-N compounds, covering the literature of the last 10 years up to July 1992.

B. TELLURIUM-NITROGEN COMPOUNDS

(i) Cyclic tellurium–nitrogen compounds

(a) Tellurium-nitrogen heterocycles

Besides the poorly characterized Te_4N_4 [4], or most likely Te_3N_4 [5], no other binary tellurium–nitrogen compounds have been described. Substituted binary and ternary Te–N heterocycles were obtained by reactions of $TeCl_4$ with $(CH_3)_3Si$-substituted amines according to [6,7]
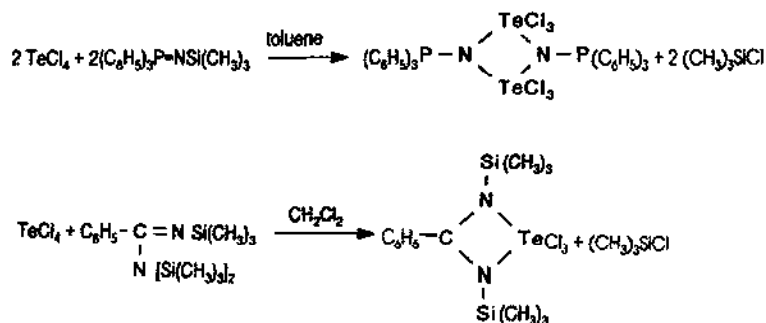
(b) Tellurium–nitrogen–chalcogen heterocycles

In recent years, Te-N heterocycles containing sulfur or selenium have been obtained using $Te(NSO)_2$ and $Se(NSO)_2$ as new non-explosive synthons. The first five-membered

ring containing a Te–N unit was formed by treatment of $Te(NSO)_2$ with $SbCl_5$ in CH_2Cl_2 [8] and elemental analysis proved the composition $Cl_5TeN_2S_2Sb$.

$$Te(NSO)_2 + SbCl_5 \xrightarrow{\;CH_2Cl_2,\ -80^\circ C\;} \overline{SNSNTeCl} \cdot Cl \cdot SbCl_3 \tag{1}$$
$$\underset{=}{1} \quad (1.1\%)$$
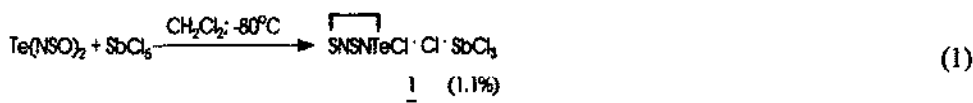
This unusual reaction can be understood in terms of oxidation of $Te(NSO)_2$ by $SbCl_5$ and elimination of SO_2. The resulting four-membered ring dimerizes to an S_4N_4 like cage, and then dissociates to give 1.
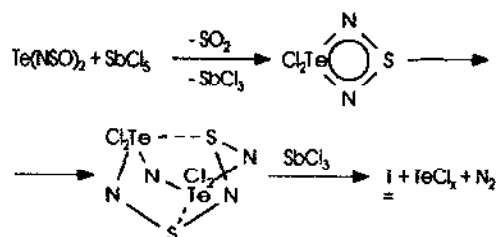
A similar reaction pathway with corresponding intermediates is postulated for the formation of $[Se_2N_2S]_2^{2+}$ from $Se(NSO)_2$ and MX_5 (see Section C(i)(b)(I)). Compound 1 was characterized by IR spectroscopy and mass spectrometry as well as X-ray crystallography. The following data were recorded. IR (NaCl): 598m, 694w, 804vs, 933w, 1011vs, 1022s, 1096m cm^{-1}. MS m/e (%): 228 (48) $SbCl_3^+$, 222 (6) $Te(NS)_2^+$, 200 (58) $TeCl_2^+$, 193 (100) $SbCl_2^+$, 176 (8) $TeNS^+$, 165 (94) $TeCl^+$, 158 (10) $SbCl^+$, 130 (28) Te^+, 121 (18) Sb^+. The structure is shown in Figs.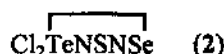 1 and 2. It consists of a five-membered ring having one exocyclic chlorine bound to tellurium. Antimony, in the oxidation state III, is coordinated by six chlorine atoms. An additional chlorine bridges Te and Sb by a three centre bond. The structure of the polymer is built up by two four-membered rings containing Sb_2Cl_2 and Te_2Cl_2 units. The alternating rings are perpendicular with respect to each other. The Te–N bond distance is 1.99 Å. Due to the low yield, the chemical behaviour of 1 has not been studied until now [8].

Recently two additional cyclic Te–N–S compounds have been synthesized. Treatment of $Se(NSO)_2$ with $TeCl_4$ provides the five-membered heterocycle

$\overline{Cl_2TeNSNSe}$ (2)

as well as the bicyclic compound $Cl_6Te_2N_2S$ (3) [9,10] according to eqn. (2).

$$Se(NSO)_2 + TeCl_4 \xrightarrow[-SO_2]{\;CH_2Cl_2\;} Cl_2TeSeN_2S + Cl_6Te_2N_2S + (Se_2N_2S)_2^{2+} (TeCl_6^-)_2 \tag{2}$$
$$\underset{=}{2}\ (24\%) \qquad \underset{=}{3}\ (27\%)$$
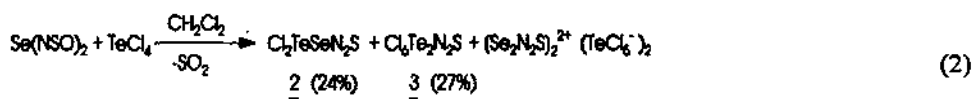
Fig. 1. Crystal structure of **1**.

For a better understanding of this complicated and by no means unique reaction, a few remarks should be made. It is well accepted that Se(NSO)₂ reacts with Lewis acids such as AsF₅, SbF₅, NbF₅ and BF₃ [11] via a cyclic dimer,

Fig. 2. Stereoscopic view of the crystal packing in **1**.

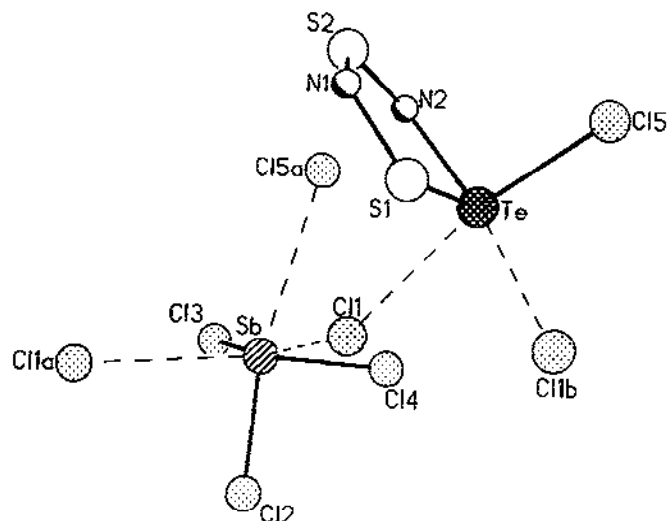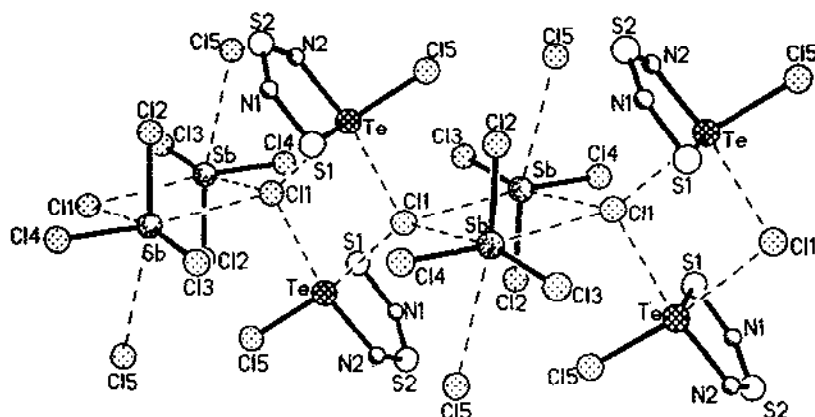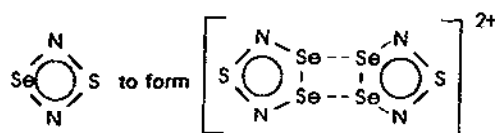another isolated product in reaction 2. At the same time, a Cl/NSO exchange can take place giving $Cl_2Te(NSO)_2$ and Cl_3TeNSO. Both molecules lose SO_2 to form

$$Cl_2Te \overset{N}{\underset{N}{\bigcirc}} S$$
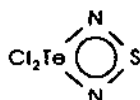
and $Cl_3TeN=S=N-TeCl_3$. The latter rearranges to the isolated derivative 3, while the former combines with

$$Se \overset{N}{\underset{N}{\bigcirc}} S$$

to give the unstable

$$\begin{array}{c} Cl_2Te\text{-----}Se \\ N \quad N \quad N \quad N \\ S\text{-----}S \end{array}$$
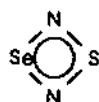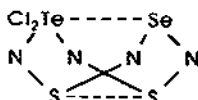
which contains the five-membered $\overline{TeNSNSe}$ ring. On losing N_2S, product 2 is formed. Scheme 1 illustrates the various reaction steps. The infrared spectrum of 2 can be compared with the well known spectrum of $\overline{Cl_2SeNSNSe}$, where the vibration at 559 cm^{-1} is assigned to $\nu(Te-N)$. The mass spectrum shows a molecular ion peak at $M^+ = 338$ confirming its covalent character. The structure has been determined by X-ray crystallographic investigation (Fig. 3). In comparison with 1, the Te–N bond distance in 2 is lengthened (2.007 Å) as it is in compound 3 (2.004 Å) which displays C_{2v} symmetry (Fig. 4). Compared with 2, the NSN angle in 3 is about 10° wider, and the geometry at tellurium can be described as pseudo-octahedral, TeX_5E (E = lone pair), where the four chlorine atoms take equatorial positions and the nitrogen atom the axial position.

Compound 3 has been characterized by IR- and Raman spectroscopy and mass spectrometry, but in contrast to 2, it does not show a molecular ion peak in the mass spectrum. The largest ion detected is $TeCl_3^+$. By reacting $TeCl_3^+AsF_6^-$ with $Se(NSO)_2$ or $TeCl_4$ with $(CH_3)_3SiNSO$, respectively, 3 becomes accessible as well [10] according to eqns. (3) and (4).

$$Se(NSO)_2 + TeCl_3^+ AsF_6^- \xrightarrow{SO_2} \underline{3} + (Se_2N_2S)_2^{2+} (AsF_6^-)_2 \tag{3}$$

$$2 TeCl_4 + 2 (CH_3)_3SiNSO \xrightarrow{CH_2Cl_2} \underline{3} + 2 (CH_3)_3SiCl + SO_2 \tag{4}$$
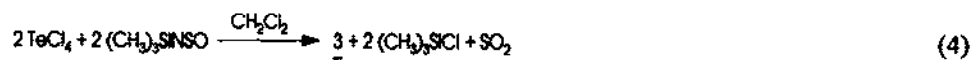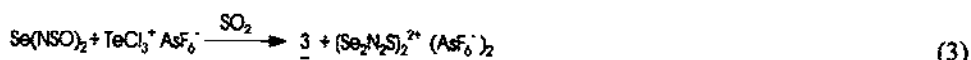
The formation of 3 can be explained by the pathway given in Scheme (1a).

Scheme 1.

Fig. 3. Crystal structure of 2 (dark-red crystals; m.p. 191°C; decomposition starting at 174°C).
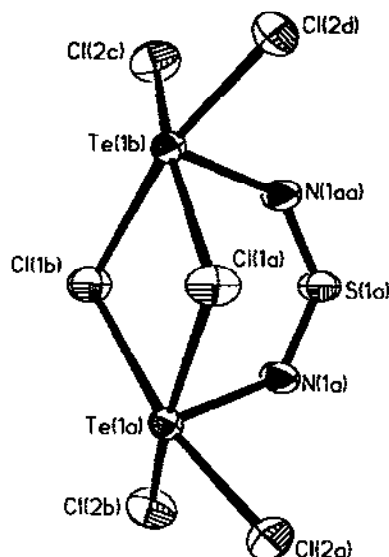
Fig. 4. Crystal structure of 3 (yellow crystals; m.p. 174°C; decomposition).

Whereas eqn. (3) gives crystalline 3 in 58% yield, eqn. (4) yields 95% of 3 as a highly air-sensitive yellow powder. Compound 3 is only slightly soluble in CH_2Cl_2, C_6H_6, C_6D_6 or toluene, but is sufficiently soluble in C_6D_6 to obtain a ^{125}Te NMR spectrum showing a $\delta(Te)$ singlet at 1728 ppm. Reaction 4 provides 3 on a preparative scale and consequently allows investigation of its chemical behaviour. The reduction of tellurium and elimination of chlorine can be easily achieved by treatment of 3 with a twofold excess of $(C_6H_5)_3Sb$ [12].

$$\underline{3} + 2\,(C_6H_5)_3Sb \xrightarrow{CH_2Cl_2} Cl_2Te_2N_2S + 2\,Cl_2Sb(C_6H_5)_3 \tag{5}$$
$$\underline{4}$$
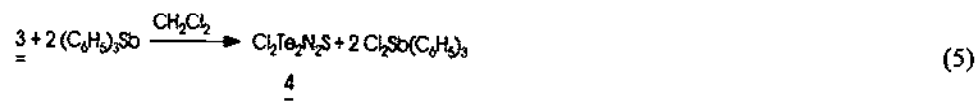
Reaction occurs within minutes, even without solvent, giving 4 as a dark red powder (m.p. 250°C; decomposition) in nearly quantitative yield. Its IR spectrum can be compared with the spectrum of 2. The vibrations assigned to $\nu(Te-N)$ are found at 519 and 585 cm^{-1}. In contrast to 2, 4 shows no molecular ion peak. Like 2, 4 is not soluble in any common organic or inorganic solvents. Therefore single crystals have not been obtained. Compound 4 is also accessible by reaction of $TeCl_4$ with $[(CH_3)_3Si]_2N-S-N[Si(CH_3)_3]_2$, according to eqn. (6).

$$TeCl_4 + [(CH_3)_3Si]_2N-S-N[Si(CH_3)_3]_2 \xrightarrow{CH_2Cl_2} \underline{4} + Me_3SiCl \tag{6}$$
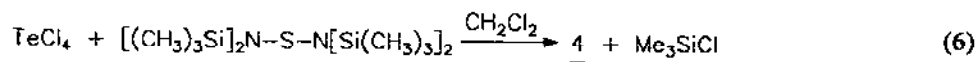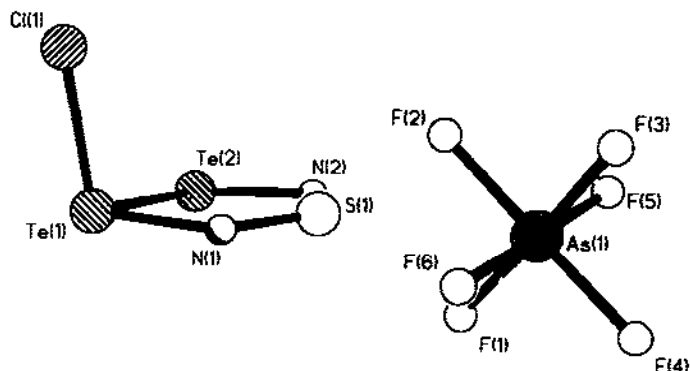
Fig. 5. Crystal structure of 5.

In the presence of excess AsF_5, **4** reacts to give its hexafluoroarsenate salt **5** (red-orange crystals), which is soluble in SO_2 [12].

$$2 \ \underset{=}{4} + 3 \, AsF_5 \xrightarrow{\ SO_2\ } 2 \, ClTe_2N_2S^+ \, AsF_6^- + AsF_3 + Cl_2 \tag{7}$$

$$\underset{=}{5}$$

Complex **5** has been characterized by IR spectroscopy and mass spectrometry, X-ray crystallography and elemental analysis. The Te–N bond distances (2.001 and 2.020 Å) confirm the character of a delocalized π-electron ring system (Fig. 5).

A compound containing Te–N bonds with a cage structure was synthesized in 1990 by reacting $TeCl_4$ with $[(CH_3)_3SiN]_2S$ [13] according to eqn. (8).

$$3 \ TeCl_4 \ + \ 3 \ (CH_3)_3SiN=S=NSi(CH_3)_3 \xrightarrow[-6(CH_3)_3SiCl]{\text{toluene}} \ (ClTeNSN)_3N \tag{8}$$

$$\underset{=}{6}$$
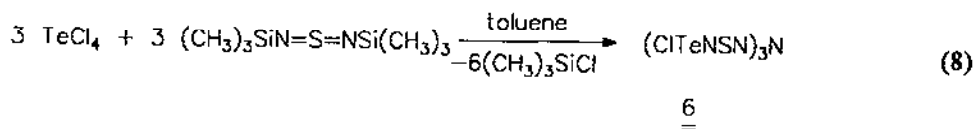
Earlier investigations of this reaction resulting in "$Te_3N_2SCl_2$" could not be verified [14]. The compound, obtained in 74% yield, is a yellow high-melting powder (m.p. 207°C), and its infrared spectrum shows six strong bands at 1120, 1090, 1060, 680, 570 and 520 cm^{-1}. Recrystallization from DMF gave crystals with the composition $(ClTeNSN)_3N \cdot$ 3DMF, but rearrangement could not be completely excluded during this procedure. Structure determination of these crystals showed that **6** has the cage structure shown in Fig. 6. The average Te–N(1) bond length is 2.06 Å and corresponds to Te–N single bond distance [15]. This also applies to the remaining six Te–N bonds with an average d(Te–N) = 2.03 Å.

The analogous reaction of TeF_4 with $[(CH_3)_3SiN]_2S$ provides the fluoro-bridged compound $(FTeNSN)_3N$ (**7**) in 51% yield [16] (eqn. (9)).

Fig. 6. Cage structure of 6.

$$TeF_4 + (CH_3)_3SiN=S=NSi(CH_3)_3 \xrightarrow[\text{2. py/toluene}]{\text{1. ether}} (FTeNSN)_3N \tag{9}$$
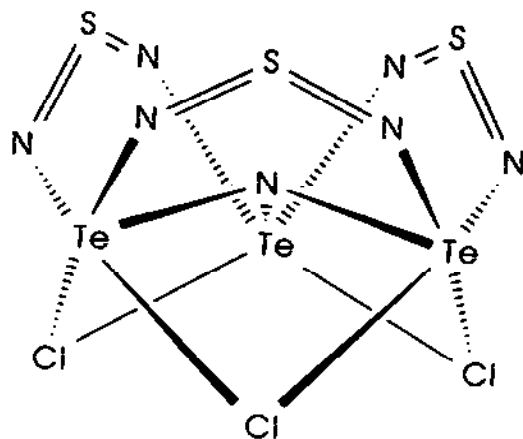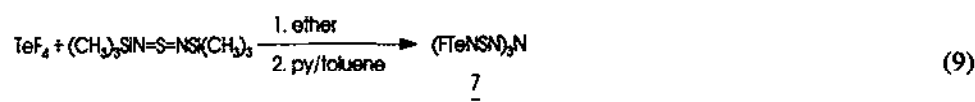
It is soluble in pyridine. ^{19}F NMR spectroscopic investigation revealed a singlet at δ −42.6 ppm. The ^{125}Te NMR shift was found at δ 1157 as a very broad signal ($\Delta\nu_{1/2}$ = 505 Hz). Further characterization was carried out by IR spectroscopy, X-ray structure analysis (Fig. 7) and elemental analysis (IR (Nujol): 1205s, 1149vs, 1056vs cm^{-1}). The mean Te–N(1) bond distance (2.03 Å) is comparable to the corresponding Te–N(1) bond length in 6 (2.06 Å), as well as the remaining six Te–N bonds, with an average d(Te–N) = 2.05 Å [16].
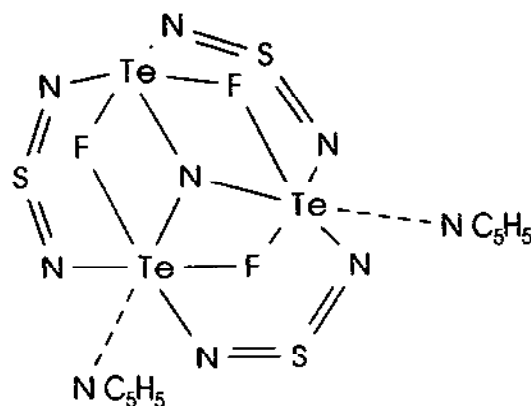
Fig. 7. Structure of 7 including two molecules of pyridine (m.p. 112°C; decomposition under mechanical shock).

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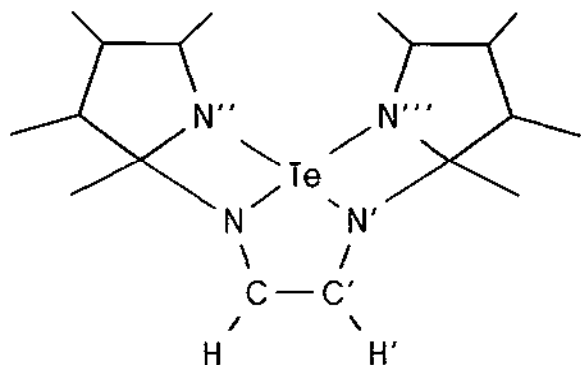
Fig. 8. Polymeric structure of 8.

(c) Tellurium–nitrogen–carbon heterocycles

Besides the cyclic Te–N–S, compounds few cyclic Te–N–C have been synthesized. In 1984, the transformation of 1,2,5-selena-diazole into 1,2,5-telluradiazole **8** was successful.

8
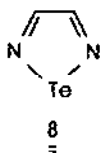
The molecules are bonded together through weak interactions between tellurium and nitrogen atoms (Fig. 8). The Te–N intermolecular distance (2.764 Å) is longer than the heterocyclic Te–N distance (2.023 Å) but shorter than the sum of the van der Waals radii of the two atoms [17]. This type of reaction could be extended to other carbon ring systems.

$$C_{14}H_8N_2Se \xrightarrow[\substack{2)\ TeCl_4 \\ 3)\ (C_2H_5)_3N}]{1)\ 2\ C_2H_5MgBr} C_{14}H_8N_2Te \qquad (10)$$

9
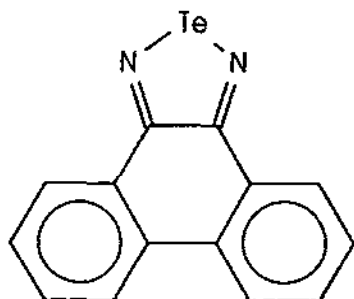
Fig. 9. Structure of **9** (m.p. 289°C).

Compound **9** was characterized by ^1H and ^{13}C NMR spectroscopy as well as by mass spectrometry. The X-ray structure analysis shows a polymeric structure presented in Fig. 9, and a Te–N single bond distance identical to d(Te–N) in **8** [18] (Fig. 9).

In 1989, the synthesis of a four-membered Te–N–C containing ring system was described. Reaction of $TeCl_4$ with N,N,N'- tris(trimethylsilyl)benzamidin provides complex **10** (eqn. (11), Fig. 10).

$$TeCl_4 + C_6H_5\text{-}C[NSi(CH_3)_3]_3 \xrightarrow[-(CH_3)_3SiCl]{} C_6H_5\text{-}C[NSi(CH_3)_3]_2TeCl_3$$
$$\underset{\text{==}}{10}$$
(11)
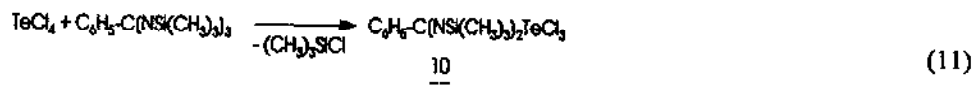
The symmetry of the tellurium atom is a distorted tetragonal-pyramid with the N1 atom in the apical position (d(Te–N1) = 2.10 Å) and the three chlorine atoms as well as the N2 atom in the equatorial positions (d(Te–N2) = 2.19 Å). On account of the sterically active lone pair, the symmetry at the tellurium atom can be regarded as pseudo-octahedral [6]. The same results were achieved by reaction 12 [19] and the compounds **10a,b** were characterized by NMR (^1H, ^{125}Te, (^{19}F)) and mass spectrometry. The crystal structure of **10a** is presented in Fig. 11.

$$TeX_4 + \text{[pyridine-NCH}_3\text{, Si(CH}_3)_3] \xrightarrow[-(CH_3)_3SiX]{} X_3Te\text{[ring-N, CH}_3]$$
(12)

$$X = Cl \quad \underset{\text{===}}{10a}$$
$$= F \quad \underset{\text{===}}{10b}$$
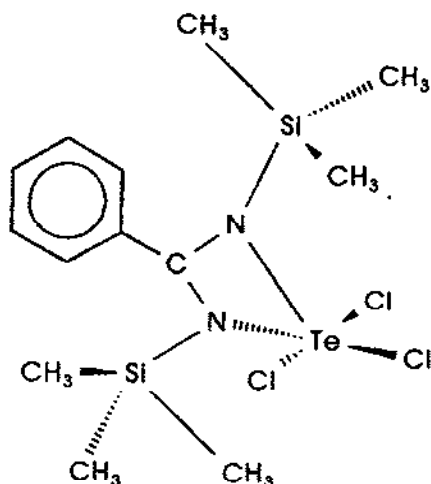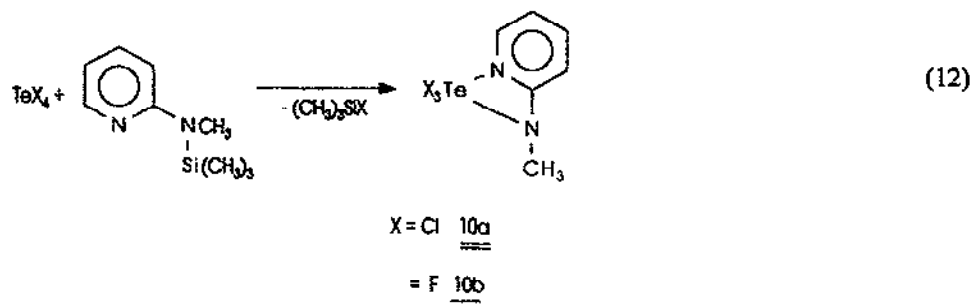
Fig 10. Structure of C_6H_5–C[NSi(CH$_3$)$_3$]$_2$TeCl$_3$ without H atoms.
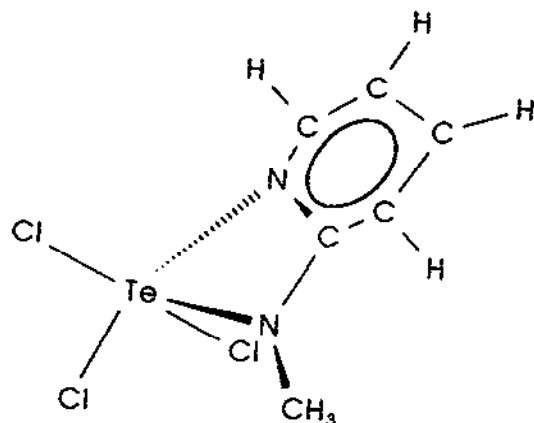
Fig. 11. Structure of $C_5H_5NTeCl_3NCH_3$.

(d) Tellurium-nitrogen-metal heterocycles

Recently the synthesis of the tellurium–nitrogen–platinum ring was described. Preparation involved reaction of "$Te_3N_2SCl_2$" with $PtCl_2[P(CH_3)_2C_6H_5]_2$ in 1,8-diazabicyclo[5,4,0]-undec-7-ene, giving $Pt(TeSN_2)[P(CH_3)_2C_6H_5]_2$, in 78% yield. It reacts with $HBF_4 \cdot Et_2O$ to give $\{Pt(TeSN_2H)[P(CH_3)_2C_6H_5]_2\}^+BF_4^-$, which was characterized by X-ray crystallography (Fig. 12). Both compounds contain air-stable PtTeSN rings. The protonated ring is isostructural to $\{Pt(SeSN_2H)[P(CH_3)_2C_6H_5]_2\}[BF_4]$ (see Section C(ii)(c)) displaying square planar coordination for the platinum centre with the metal bonded to the tellurium of the $TeSN_2H^-$ anion [99].

In summary, all cyclic Te–N compounds are stable in comparison to Te_4N_4. The number of systems elucidated are small in comparison with those in S–N and Se–N
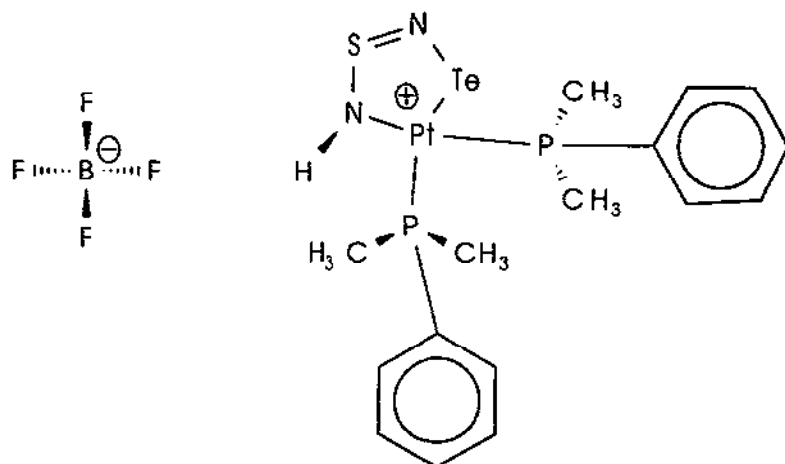
Fig 12. Structure of $Pt(TeSN_2H)[P(CH_3)_2C_6H_5]_2$.

heterocyclic chemistry. The ability of S–N and Se–N rings to form stabilized π-bonding (aromatic rings) does not account to the same extent for Te–N rings. No Te–N double or triple bonds have been observed so far. Instead stabilization takes place by forming multi-electron-multicentre bonds as in $Cl_6Te_2N_2S$ (**3**), $(ClTeSN)_3N$ (**6**) and $(FTeSN)_3N$ (**7**).

Cation $\overline{ClTeNSNTe^+}$, which has shortened Te–N bonds, contains the only delocalized π-system similar to $\overline{ClENSNE}$ (E = S, Se).

(ii) Tellurium–nitrogen compounds

(a) Te^{II}–N compounds

It was generally accepted that compounds containing Te–N bonds are unstable, and descriptions of violent explosions by Te_4N_4 [4] or Te_3N_4 [5] deterred most chemists from intensive investigations in this field. Therefore, the preparation of the first stable and non-explosive Te^{II}–N-compound was not reported until 1989. The attempted preparation of the $Se(NSO)_2$ analogue, $Te(NSO)_2$ was realized when $(^tBuMe_2Si)_2Te$ was treated with $ClNSO$ [20] according to eqn. (13).

$$(t\text{-}BuMe_2Si)_2Te + 2\ ClNSO \xrightarrow{\ CH_2Cl_2\ } Te(NSO)_2 + 2\ t\text{-}BuMe_2SiCl$$
$$[+ S(NSO)_2]$$
$$\underline{\mathbf{11}}$$

(13)
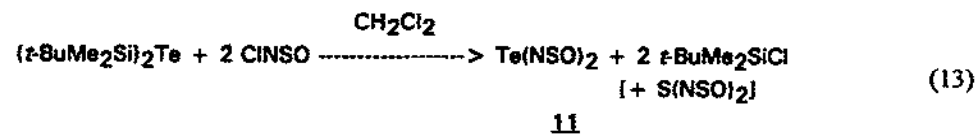
The red crystals were sublimed at 50°C/10^{-3} Torr in 36% yield, and are extremely sensitive to moist air. X-Ray diffraction studies (Fig. 13) showed that **11** is isomorphous to $Se(NSO)_2$ [21] and $S(NSO)_2$ [22]. The Te–N-bond distance (2.039 Å) corresponds to a Te–N single bond. It was further characterized by its mass and IR spectrum. The mass spectrum shows an M^+ ion which was identified by its isotopic pattern. Further fragments are: $TeNS_2O^+$, $TeNS_2^+$, TeN_2S^+, $TeNS^+$, TeS^+, TeN^+, Te^+, $S_2N_2^+$, S_2^+. Decomposition occurs on heating above 132°C and a black solid is formed which explodes violently on further heating. Solubility of **11** in CH_2Cl_2 is sufficiently high for a ^{125}Te NMR spectrum [$\delta(Te)$ 1273 (s)].

Fig. 13. Molecular structure of **11**.

In 1990, the preparation of another non-explosive Te^{II}–N compound was reported. Reaction of $TeCl_4$ with $LiN(SiMe_3)_2$ provides $Te[N(SiMe_3)_2]_2$ in 50% yield.

$$4\ LiN(SiMe_3)_2 + TeCl_4 \xrightarrow[\substack{\text{toluene/}\\ \text{hexane;}\ -70^\circ C\\ -LiCl}]{} Te[N(SiMe_3)_2]_2 \tag{14}$$

$$\underset{\underset{=}{12}}{}$$
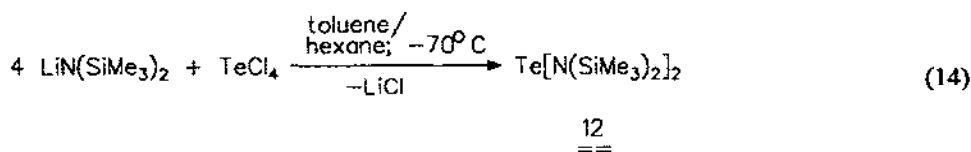
It has been characterized spectroscopically and by elemental analysis. Sublimation provides orange crystals, suitable for an X-ray structure determination. The mean Te–N bond length of 2.049 Å [23] is comparable to that in **11**. The remarkable volatility of Te^{II}–N compounds is also exhibited by CF_3TeNSO. It is accessible by treatment of a $(CF_3Te)_2$ mixture with I_2 and $Hg(NSO)_2$ according to eqn. (15).

$$(CF_3Te)_2 + I_2 + Hg(NSO)_2 \xrightarrow[\text{THF}]{\text{CHCl}_3} \underset{\underset{=}{13}}{2\ CF_3TeNSO + HgI_2} \tag{15}$$

$$38\%$$
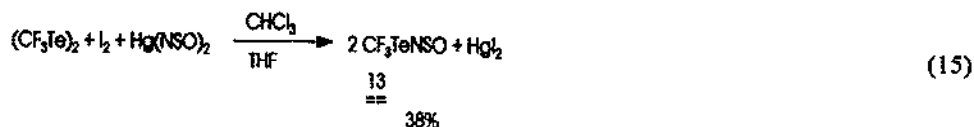
The molecule (m.p. 15°C) was characterized by mass spectrometry and IR and NMR spectroscopy: ^{19}F: δ –29.1 (s); ^{13}C: δ 111.1 (q); ^{125}Te: δ 1908 (s, br); IR (gas): 1217m, 1155s, 1099vs, 731w, 596vw cm^{-1}. MS: M^+, CF_3Te^+, $TeNSO^+$, $TeSN^+$, TeS^+, TeN^+, Te^+, CF_3^+, CF_2^+, SO^+, SN^+, S^+ [24]. Stable Te^{II}–N compounds may also be obtained by reaction of $[Me_3Si]_3CTeI$ with AgNCO, AgN_3 or K_2N_2S as shown in eqns. (16)–(18).

$$[Me_3Si]_3CTeI + AgNCO \longrightarrow [Me_3Si]_3CTeNCO + AgI \tag{16}$$

$$[Me_3Si]_3CTeI + AgN_3 \longrightarrow [Me_3Si]_3CTeN_3 + AgI \tag{17}$$

$$2\ [Me_3Si]_3CTeI + K_2N_2S \longrightarrow [[Me_3Si]_3CTeN]_2S + 2KI \tag{18}$$
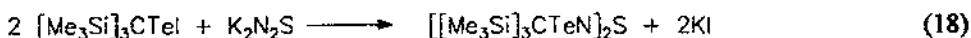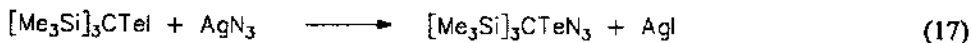
^1H NMR and mass spectroscopic data (tabulated below) were reported but no other data were provided [25].

	$\delta(CH_3)$	MS
$[Me_3Si]_3CTeNCO$	0.18 (s)	M^+, $[M - NCO]^+$
$[Me_3Si]_3CTeN_3$	0.17 (s)	M^+, $[Me_3Si]_3CTe^+$
$[[Me_3Si]_3CTeN]_2S$	0 30 (s)	M^+, $[M - [Me_3Si]_3CTe]^+$, $[Me_3Si]_3CTe^+$

(b) Te^{III}–N compounds

   X-Ray diffraction studies have proved the existence of the first Te^{III} species (Fig. 14). The reaction of **12** with $AgAsF_6$ in CH_2Cl_2 yields black crystals consisting of the radical cation **14** according to eqn. (19).
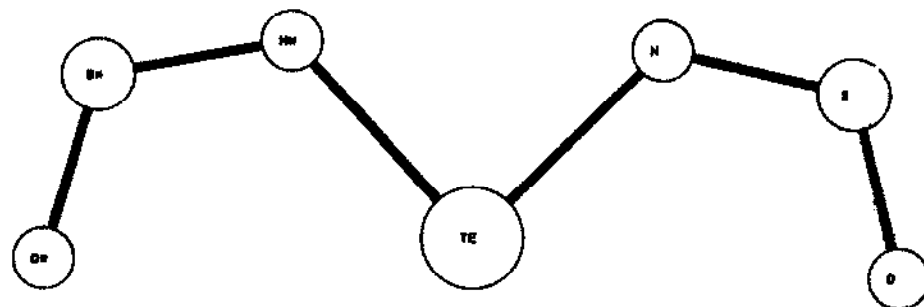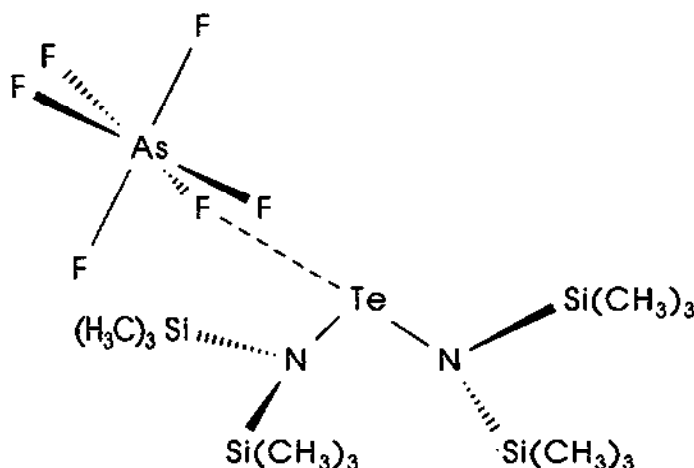
Fig. 14. Molecular structure of 14.

$$\underset{==}{12} + Ag^+ \; AsF_6^- \xrightarrow{CH_2Cl_2} \{(((CH_3)_3Si)_2N)_2Te\}^+ \; (AsF_6)^- + Ag^0 \tag{19}$$

$$\underset{==}{14}$$
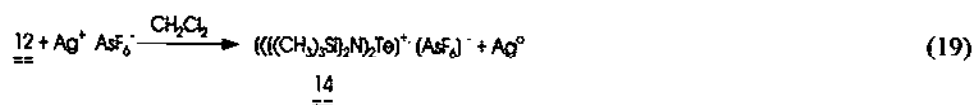
The Te–N bond distance (1.966 Å) is substantially shorter than in 12 (2.049 Å) and was interpreted as a partial Te–N double bond. Furthermore, the radical cation was character-ized by ^{1}H NMR [δ(CH$_3$) 0.45 ppm], ESR (g = 2.0; $\Delta\omega_{1/2}$ = 15 G) and UV/vis spectros-copy (λ_{max} = 615 nm) [26].

(c) Te^{IV}–N compounds

The first acyclic Te^{IV}–N species was described in 1967. It was formed by am-monolysis of Te(C$_6$H$_5$)$_2$ in the presence of KNH$_2$ providing K$_2$[Te(NH)$_3$] [5] according to eqn. (20).

$$7 \; Te(C_6H_5)_2 + 10 \, KNH_2 + 2 \, NH_3 \longrightarrow 4 \, K_2\{Te(NH)_3\} + K_2Te_3 + 14 \, C_6H_6 \tag{20}$$

Starting from TeCl$_4$ and (CH$_3$)$_3$SiN$_3$, it is possible to replace one or two chlorine atoms by azide groups (eqn. (21)).

$$TeCl_4 + n \; Me_3SiN_3 \longrightarrow Cl_{4-n}Te(N_3)_n + n \; Me_3SiCl \tag{21}$$

$$n = 1, \; 2$$
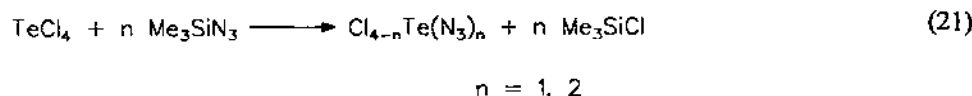
Both compounds are characterized by IR spectroscopy and elemental analysis. As ex-pected, the azides are violently explosive [27]. This does not apply to the first binary Te–N cation Te(N$_3$)$_3^+$, however, if the preparation is not carried out carefully, other prod-ucts formed explode violently. It is prepared by reaction of Te$_4$(SbF$_6$)$_2$ with KN$_3$ in liquid
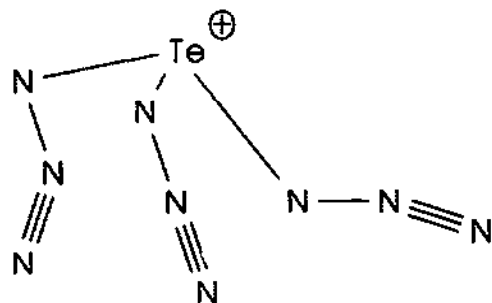
Fig. 15. Structure of Te(N₃)₃⁺.

SO₂. IR and Raman spectroscopic data for the colourless crystals are as follows: IR (Nujol): 3330w, 3280w, 2425w, 2410w, 2390w, 2360w, 2145s, 2130s, 2100s, 1299m, 1217m, 1197s, 1175m, 1093w, 1028w, 728w, 685w, 659s, 636w, 584w, 549s, 460w, 440m, 426s cm⁻¹. Ra (single crystal): 2165w, 2149m, 2128w, 2114w, 2102w, 1196w, 680w, 656w, 638m, 566w, 456vs, 432s, 266w cm⁻¹. X-Ray investigations showed that the average d(Te–N) = 1.994 Å is in good agreement with a Te–N single bond distance (1.99 Å) (Fig. 15) [28].

Further stabilization of the Te–N bond is achieved when tellurium is coordinated to sterically demanding ligands, e.g. (C₆H₅)₃TeX; X = NCO, NCS (Fig. 16) [29]. The struc-
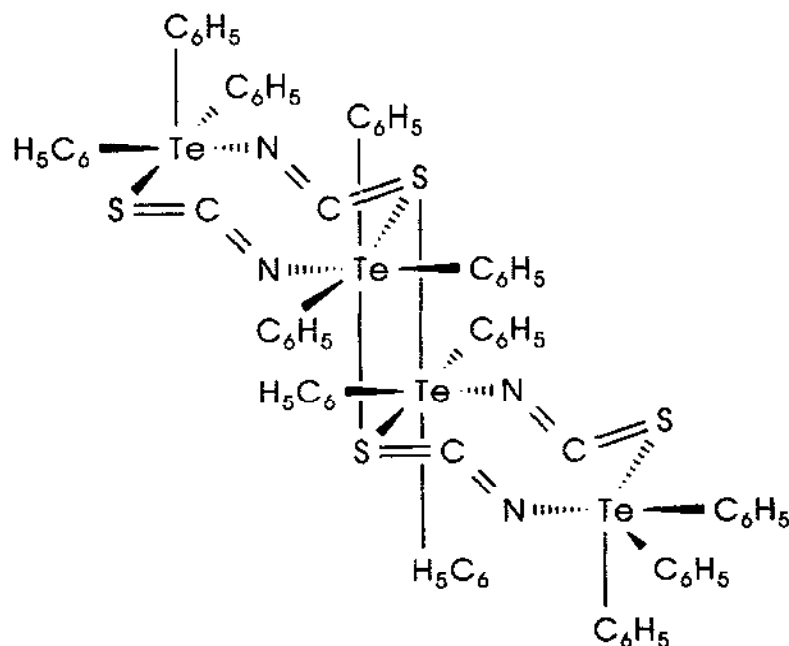
Fig 16. Structure of Ph₃TeNCS tetramer in [Ph₃TeNCS]₄[Ph₃TeNCS]₂ [30].
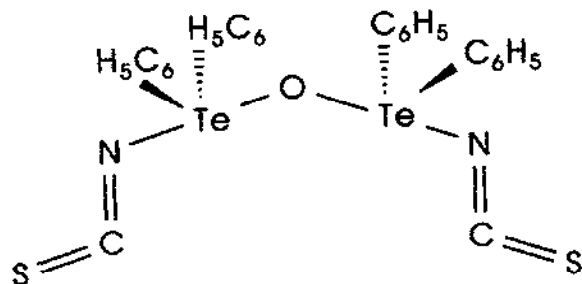
Fig. 17. Structure of $Ph_2Te(NCS)$–O–$Te(NCS)Ph_2$.

ture of an oxygen-bridged moiety of $Ph_2Te(NCS)$–O–$Te(NCS)Ph_2$ was reported in 1977 [31] (Fig. 17).

$RTeCl_3$ derivatives are also adequate precursors for the preparation of stable Te^{IV}–N compounds. The elimination of Me_3SiCl is the driving force in the reaction of $RTeCl_3$ with Me_3Si–N-containing compounds. This metathesis turned out to be a simple method for preparing substances with a $Te(Cl_2)$–N moiety according to eqns. (22) and (23).

$$R^1\text{-TeCl}_3 + R^3\text{=NSiMe}_3 \longrightarrow R^1\text{TeCl}_2\text{N=}R^3 + Me_3SiCl \tag{22}$$

$$TeCl_4 + 2\,R^2\text{=NSiMe}_3 \longrightarrow R^2\text{=N-TeCl}_2\text{-N=}R^2 + 2\,Me_3SiCl \tag{23}$$

$$R^1\text{=MeO}-\text{\textcircled{}}- \ ; \ R^2\text{=PPh}_3; \quad R^3\text{=PPh}_3, \ Me_2\overset{\overset{\displaystyle O}{\|}}{S}\text{=N SiMe}_3$$
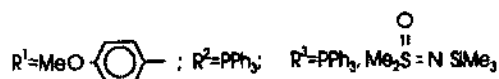
The Te–N bond lengths in $Ph_3P=N$–$TeCl_2$–$N=PPh_3$ (1.912 Å) (Fig. 18) and $MeOC_6H_4TeCl_2$–$NPPh_3$ (1.918 Å) (Fig. 19) are substantially shorter than a Te–N single bond distance, and electronic stabilization effects are thought to be responsible. Both compounds are also fully characterized by IR (^{1}H and ^{31}P) NMR spectroscopy and mass spectrometry [32].
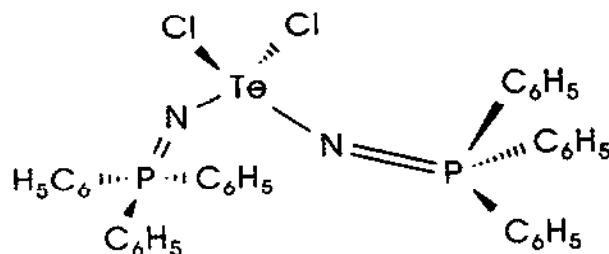
Fig. 18. Structure of $(C_6H_5)_3PNTeCl_2NP(C_6H_5)_3$.
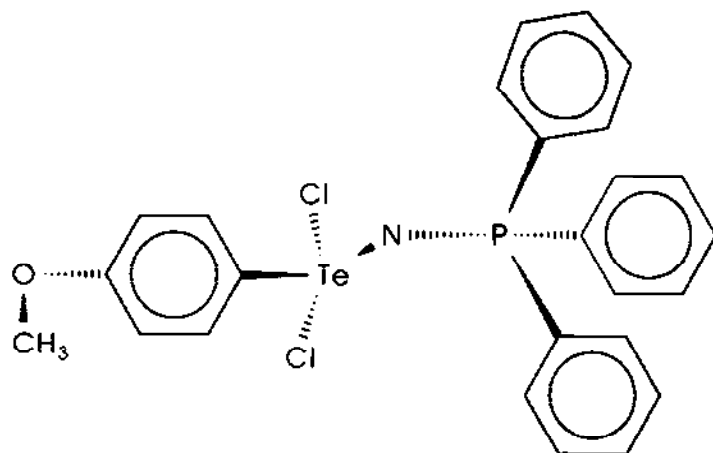
Fig. 19. Structure of MeOC$_6$H$_4$TeCl$_2$NP(C$_6$H$_5$)$_3$.

(d) Te^{VI}–N compounds

   This chemistry has developed in the past 20 years using the starting material TeF$_6$. Since the description of the first TeF$_6$ adducts with tertiary amines in 1957 [33], no further investigation was made until 1971, when reaction of TeF$_6$ with silylamines was studied [34], producing dialkylaminotelluriumpentafluorides TeF$_5$NR$_2$ (R = CH$_3$, C$_2$H$_5$, C$_4$H$_8$). Using an excess of silylamine the bis-substituted derivative TeF$_4$[N(CH$_3$)$_2$]$_2$ is formed instead. Mixed derivatives are also known, namely TeF$_5$N(CH$_3$)C$_2$H$_5$, TeF$_4$-[N(CH$_3$)$_2$]N(C$_2$H$_5$)$_2$, TeF$_5$N(CH$_3$)Si(CH$_3$)$_3$ and TeF$_5$N(CH$_3$)CH$_2$CH$_2$N(CH$_3$)Si(CH$_3$)$_2$F, respectively. Most of these compounds have been characterized by ^{1}H and ^{19}F NMR, IR and Raman spectroscopy as well as by mass spectrometry [34]. In 1973, the synthesis of aminotelluriumpentafluoride was successful. *N*-Trimethylsilylaminotelluriumpentafluoride, (CH$_3$)$_3$SiNHTeF$_5$, accessible by reaction of [(CH$_3$)$_3$Si]$_2$NH with TeF$_6$, reacts with HF to give TeF$_5$NH$_2$ [35]. Thus, a promising starting material for development of TeF$_5$N chemistry was now available. Both compounds turned out to be relatively stable against HF elimination [36].

   An alternative route to build up F$_5$TeN systems is the reaction between (CH$_3$)$_3$SiN(H)TeF$_5$ plus PF$_5$ and the photolytic addition of TeF$_5$Cl to nitriles (eqns. (24) and (25)).

$$2(CH_3)_3SiNHTeF_5 + PF_5 \longrightarrow F_5Te-N=PF_3 + H_2NTeF_5 + 2(CH_3)_3SiF \qquad (24)$$

$$TeF_5Cl + ClCN \xrightarrow{\text{h}\nu} F_5TeN=CCl_2 + Cl_2C=N-N=CCl_2 + TeF_4 + TeF_6 \qquad (25)$$
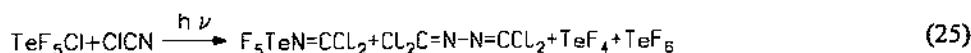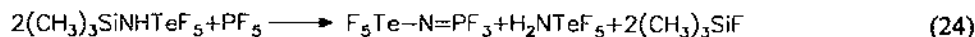
Reaction of F$_5$TeN=CCl$_2$ with HF, CsF or HgF$_2$ gives other derivatives of which the Hg[N(CF$_3$)TeF$_5$]$_2$ offers the highest synthetic potential.

$$2\ F_5TeNCCl_2\ +\ 3\ HgF_2\ \xrightarrow{60\ ^\circ C}\ Hg[N(CF_3)TeF_5]_2\ +\ 2\ HgCl_2 \tag{26}$$
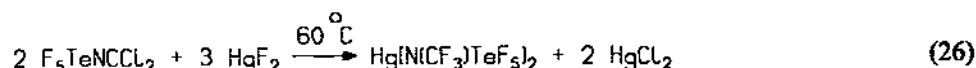
Cleavage of $Hg[N(CF_3)TeF_5]_2$ with halogens or interhalogens, e.g. F_2, ClF, Br_2, ICl, provides $F_5TeN(X)CF_3$ compounds (X = F, Cl, Br, (I)). A variety of TeF_5NCF_3 derivatives are prepared starting from the haloamines $F_5TeN(X)CF_3$. Photolysis of the N-chloro compound gives $(TeF_5)_2NCF_3$ in low yield (eqn. (27)).

$$2\ TeF_5N(Cl)CF_3\ \xrightarrow{h\nu}\ (TeF_5)_2NCF_3\ +\ Cl_2\ +\ \dots \tag{27}$$
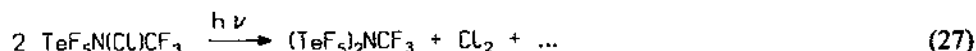
In the presence of SF_5Cl, $F_5TeN(SF_5)CF_3$ is also obtained so it is quite evident that the radical reaction proceeds through several steps [37]. Products, reactions, characterization methods and physical properties are summarized in Table 1. Besides the reaction of $Cl_2S=NTeF_5$ with $(CF_3CO)_2O$, F_5TeNSO is also accessible by treatment of $F_5TeOE(CH_3)_3$ with NSF (E = Si, Sn).

$$F_5TeOE(CH_3)_3\ +\ NSF\ \longrightarrow\ F_5TeNSO\ +\ (CH_3)_3EF\ \ (+\ polymers) \tag{28}$$
$$E\ =\ Si,\ Sn$$
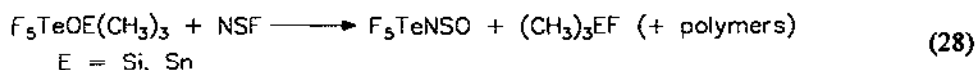
In addition, reaction of $(F_5TeO)_3B$ with NSF gives $F_5TeNSNTeF_5$ [39].

$$(F_5TeO)_3B+NSF\ \longrightarrow\ F_5TeOSN+F_5TeNSO+F_5TeNSNTeF_5(+\ BF_3) \tag{29}$$
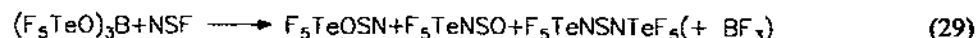
$F_5TeNSNTeF_5$ was characterized by IR, Raman and ^{19}F NMR spectroscopy.

$Cl_4W=NTeF_5$ was the first compound containing a F_5TeN group to be examined by X-ray diffraction methods. The Te–N bond distance (1.98 Å) corresponds to a Te–N single bond distance [36] (Fig. 20). The simple preparation of $Cl_4W=NTeF_5$ could not be extended to other chlorides, nevertheless the synthesis of further fluorides were successful.

$$2(CH_3)_3Si-NHTeF_5+MF_6\ \longrightarrow\ 2(CH_3)_3SiF+H_2NTeF_5+F_4M=NTeF_5 \tag{30}$$

$$M\ =\ W,\ Mo$$

$$VF_5\ +\ H_2NTeF_5\ \longrightarrow\ F_3V=NTeF_5\ \cdot\ 2HF \tag{31}$$
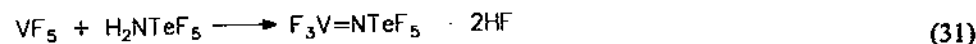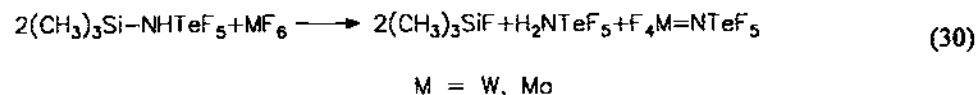
Chlorometal derivatives are accessible by fluorine/chlorine interchange with BCl_3.

$$F_4Mo=NTeF_5\ \xrightarrow[-BF_3]{BCl_3}\ Cl_4Mo=NTeF_5 \tag{32}$$

$$F_3V=NTeF_5\ \xrightarrow[-BF_3]{BCl_3}\ Cl_3V=NTeF_5 \tag{33}$$

TABLE 1

Preparation, characterization methods and physical properties of F_5TeN compounds

Product	Reactants	Yield (%)	m.p. (°C)	b.p. (°C)	IR	Ra	NMR spectrum	Mass	Remarks
F_5TeNCO [34]	COF_2, $(CH_3)_3SiNHTeF_5$	25	–95	39	Yes	Yes	^{19}F	No	
–NSO [36]	Cl_2SNTeF_5, $(CF_3CO)_2O$	68	–24.6	–	Yes	Yes	^{19}F	Yes	
–NSF$_2$ [36]	SF_4, $(CH_3)_3SiNHTeF_5$	40	–78	–	Yes	Yes	^{19}F	No	
–NSCl$_2$ [36]	BCl_3, F_5TeNSF_2	85	16	–	No	Yes	^{19}F	No	
–NSeF$_2$ [36]	SeF_4, $(CH_3)_3SiNHTeF_5$	–	–	–	No	No	^{19}F	No	Mixture of H_2NTeF_5 and $F_5TeNSeF_2$
–NSeCl$_2$ [36]	$SeCl_4$, H_2NTeF_5	82	16	–	Yes	Yes	^{19}F	No	
–NPF$_3$ [36]	PF_5, $(CH_3)_3SiNHTeF_5$	75	–60	54	Yes	Yes	^{19}F, ^{31}P	No	
–NPCl$_3$ [36]	PCl_5, H_2NTeF_5	77	23.4	84	No	Yes	^{19}F, ^{31}P	No	
–NCl$_2$ [36]	ClF, $(CH_3)_3SiNHTeF_5$	72	–79	–	No	Yes	^{19}F	Yes	
–NSF$_2$O [36]	SOF_4, $(CH_3)_3SiNHTeF_5$	83	<–78	–	Yes	Yes	^{19}F	Yes	
–NClSi(CH$_3$)$_3$ [36]	Cl_2NTeF_5, $(CH_3)_3SiBr$	55	–	–30 (10^{-2} mbar)	–	–	^{19}F, ^1H	Yes	
–NHC(O)OCH$_3$ [36]	CH_3OH, F_5TeNCO	25	77	–	No	Yes	^{19}F, ^1H	No	
–NHC(O)OCH$_3$ [38]	CH_3COOH, F_5TeNCO	70	102–102.5	–	Yes	Yes	^{19}F, ^1H	Yes	
–NC(Cl)CH$_3$ [38]	PCl_5, $F_5TeNC(O)CH_3$	26	–	–	Yes	No	^{19}F, ^1H	Yes	
–NC(H)N(CH$_3$)$_2$ [38]	$HC(O)N(CH_3)_2$, F_5TeNCO	–	–	–	Yes	No	^{19}F, ^1H	Yes	Not pure

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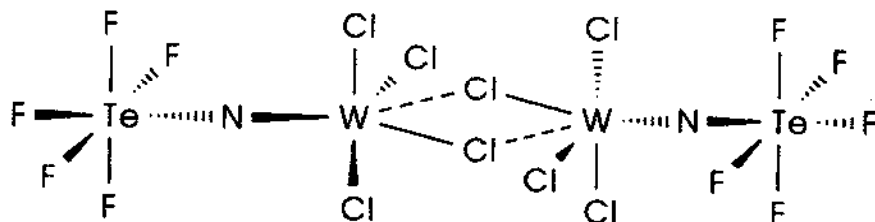| Compound	Reagents						NMR		Comments
-NC(H)C$_6$H$_5$ [38]	C$_6$H$_5$C(O)H, F$_5$TeNCO	—	—	—	Yes	No	^{19}F, ^{1}H	Yes	Not pure
-NCCl$_2$ [37]	TeF$_5$Cl, ClCN	32	—	—	Yes	Yes	^{19}F	Yes	
-NC(Cl)CF$_3$ [37]	TeF$_5$Cl, CF$_3$CN	—	—	—	Yes	No	^{19}F	Yes	
-NHCF$_3$ [37]	HF, TeF$_5$NCCl$_2$	90	—	62.3	Yes	Yes	^{19}F, ^{1}H	Yes	
-NC(Cl)OCH$_3$ [37]	F$_5$TeNCCl$_2$, NaOCH$_3$	3	16–18	—	Yes	Yes	^{19}F, ^{1}H	Yes	
-NC(OCH$_3$)$_2$ [37]	F$_5$TeNCCl$_2$, NaOCH$_3$	58	76–78	—	Yes	Yes	^{19}F, ^{1}H; ^{13}C	Yes	
-NCF$_2$ [37]	Hg[N(CF$_3$)TeF$_5$]$_2$ (CH$_3$)$_3$SiCl	48	—	50	Yes	Yes	^{19}F	Yes	
-NC(F)N(CF$_3$)TeF$_5$ [37]	F$_5$TeNCCl$_2$, HF	20	5–7	—	Yes	Yes	^{19}F	Yes	
-NHC(F)NCF$_3$ [37]	F$_5$TeNHCF$_3$	49	2–3	—	Yes	Yes	^{19}F, ^{1}H	Yes	
-N(F)CF$_3$ [37]	Hg[N(CF$_3$)TeF$_5$]$_2$, F$_2$	62	—	28.9	Yes	Yes	^{19}F	Yes	
-N(Cl)CF$_3$ [37]	Hg[N(CF$_3$)TeF$_5$]$_2$, ClF	95	—	59.8	Yes	Yes	^{19}F	Yes	
-N(Br)CF$_3$ [37]	Hg[N(CF$_3$)TeF$_5$]$_2$, Br$_2$	68	—	86.7	Yes	Yes	^{19}F	Yes	
-N(I)CF$_3$ [37]	Hg[N(CF$_3$)TeF$_5$]$_2$, ICl	—	—	—	No	No	^{19}F	No	Not pure
-N(CF$_3$)C(O)—CH$_3$ [37]	Hg[N(CF$_3$)TeF$_5$]$_2$, CH$_3$C(O)Br	73	-41	—	Yes	Yes	^{19}F, ^{1}H; ^{13}C	Yes	
-N(CF$_3$)TeF$_5$ [37]	TeF$_5$N(Cl)CF$_3$	3	—	—	Yes	No	^{19}F	Yes	Photolyzed by low pressure Hg lamp
-N(CF$_3$)SF$_5$ [37]	TeF$_5$N(Cl)CF$_3$, SF$_5$Cl	—	—	—	Yes	No	^{19}F	Yes	
-N(CF$_3$)CH$_2$—CH$_2$Br [37]	TeF$_5$N(Br)CF$_3$, C$_2$H$_4$	91	-18	—	Yes	Yes	^{19}F, ^{1}H	Yes	
-NWCl$_4$ [36]	WCl$_6$, (CH$_3$)$_3$SiNHTeF$_5$	65	136–145	—	No	Yes	^{19}F	No	

Fig. 20. Structure of Cl₄W=NTeF₅.

All of these compounds have been characterized by IR and ^{19}F NMR spectroscopy and mass spectrometry as well as by elemental analysis [40].

The synthesis of acyclic Te–N single bonded systems in the oxidation states II, III, IV, and VI is dependent on the availability of suitable starting materials. Compared with the high number of well characterized acyclic S–N and Se–N compounds, only a few Te–N systems have been synthesized. In contrast to sulfur and partly selenium, stable tellurium halides only exist in the oxidation states IV and VI. This and the lower stability of the Te–N bond are responsible for the fact that Te^{II}–N and Te^{III}–N compounds are rare. As already pointed out for Te–N-containing ring systems, acyclic Te–N compounds are not explosive except at high temperatures. Therefore, materials such as $Te(NSO)_2$ and $[(CH_3)_3Si]_2NTeN[Si(CH_3)_3]_2$ are good synthons for exploring new areas of Te–N chemistry. Up to now, only F_5TeN derivatives have been investigated intensively. The analogues to $F_3S \equiv N$ or $FS \equiv N$, $F_3Te \equiv N$ or $FTe \equiv N$ have not yet been prepared. Since it was possible to synthesize and characterize the first compound with a Te=C double bond, namely $F_2C = Te$ [41], one can also expect successful attempts for the preparation of substances with Te–N multiple bonds in the near future.

C. SELENIUM–NITROGEN COMPOUNDS

Although the synthesis of binary chalcogen–nitrogen compounds such as S_4N_4 [42] and Se_4N_4 [43] were already accomplished in the middle of the 19th century, little attention was paid to their chemistry. However, the discovery of super conductivity of polymeric $(SN)_x$ at low temperatures [44] initiated more intensive investigations. Synthesis and chemical properties of new S–N compounds were studied and in the last 20 years, preparations of numerous representatives, including many ring systems, have been reported [45–50]. Their stability was explained by additional π-bonding. Some binary cationic ring species exhibit properties of heteroaromatic systems (e.g. they are almost planar). Others form cage-like structures stabilized by chalcogen–chalcogen bonding interactions [51–53]. However, compounds with superconducting properties like $(SN)_x$ $[(SeN)_x$ and $(TeN)_x]$ have not yet been synthesized.

The first part of this section deals with new developments for the preparation of cyclic –Se–N compounds, neglecting Se–N–C heterocycles, followed by a second part

which describes progress in acyclic Se–N chemistry including compounds containing Se–N double bonds.

(i) Cyclic selenium–nitrogen compounds

(a) Binary cyclic selenium–nitrogen compounds

(I) Tetraseleniumtetranitride. This compound was synthesized for the first time in 1859 by reacting $SeCl_4$ with NH_3 [43]. In general, Se_4N_4 is accessible by ammonolysis of SeO_2, $SeCl_4$, $SeBr_4$, or $(C_2H_5O)_2SeO$. These preparations are summarized in the literature [54]. The reaction between SeO_2 and liquid NH_3 in an autoclave at 70–80°C is faster and superior [55] to ammonolysis of $SeCl_4$ with NH_3 [56] and provides 25% yield. Replacing SeO_2 by $SeCl_4$ or $SeBr_4$ provides increased yields of 60 or 75%, respectively [55]. In recent years, a new route to Se_4N_4 was described starting from $Se[N(SiMe_3)_2]_2$ and $SeCl_4$ [11] together with slight modifications [57].

The outstanding property of Se_4N_4 is its explosiveness. Pure and dry orange or red Se_4N_4 can explode violently on heating or mechanical shock. Therefore, only small amounts should be stored under $CHCl_3$ or CCl_4. Se_4N_4 is insoluble in water and common organic solvents [4]. The standard heat of formation is $\Delta H_{298} = 163 \pm 3$ kcal/mol [formation of solid from the elements; mean Se–N bond energy 59 ± 10 kcal/mol (gaseous Se_4N_4)] [58]. The structure of Se_4N_4 was determined by X-ray crystallographic studies and like S_4N_4, consists of discrete cage-like molecules (Fig. 21). The average Se–N bond distance of 1.79 Å exhibits partially double bond character (Pauling's single bond distance is 1.86 Å). The intramolecular Se···Se distances (2.75 Å) are shorter than the corresponding sum of the van der Waals radii (4.00 Å) and should be interpreted as weak bonding interactions. In contrast to S_4N_4, tetraselenium tetranitride contains intermolecular SeN···NSe contacts (2.96–3.45 Å). Several authors believe them to be responsible for the insolubility of Se_4N_4 [59,60].

The mass spectrum of Se_4N_4 was described revealing Se_2N^+ as a base peak and the M^+ peak [56]. Earlier infrared spectroscopic data [61] were re-investigated in 1988 and 1990. The novel infrared [62] and Raman [58] spectra are in excellent agreement with a molecular structure of slightly deformed D_{2d} symmetry containing Se–N-bonds with a bond order between 1 and 2 and weak intramolecular Se···Se contacts. Absorptions and assignments are given in Table 2.
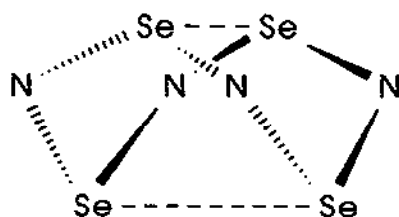

Fig. 21. Molecular structure of Se_4N_4 [59].

TABLE 2

IR [61] and Raman spectra [62] of Se_4N_4: assignments based on D_{2d} symmetry

Absorption (cm^{-1})		Intensity	Assignment
621	Ra	2	ν_1, ν(Se–N), (A_1)
318	Ra	3	ν_2, δ(Se–Se–N), (A_1)
154	Ra	10	ν_3, ν(Se–Se), (A_1)
534	IR	m	ν_8, ν(Se–N), (B_2)
310	IR	m	ν_9, δ(Se–Se–N), (B_2)
147	IR	m	ν_{10}, ν(Se–Se), (B_2)
800	IR	s ⎫	
788	IR	s ⎬	ν_{11}, ν(Se–N), (E)
787	IR	<1 ⎭	
570	IR	vs	ν_{12}, ν(Se–N), (E)
425	IR	vs	ν_{13}, δ(Se–Se–N), (E)
270	IR	m ⎫	
260	IR	s ⎬	ν_{14}, δ(Se–Se–N), (E)
261	Ra	1 ⎭	

Due to its explosiveness and insolubility, the synthetic potential of Se_4N_4 was not realized until 1988 when Dehnicke et al. were able to prepare new SeN species using Se_4N_4 as a starting material. The chloroselenonitrene complexes $[Cl_4W(NSeCl)]_2$ [63] and $[Cl_4MoNSeCl]_2$ [64] were prepared by reacting Se_4N_4 with WCl_6 or $[MoCl_5]_2$ in CH_2Cl_2 according to eqn. (34).

(34)
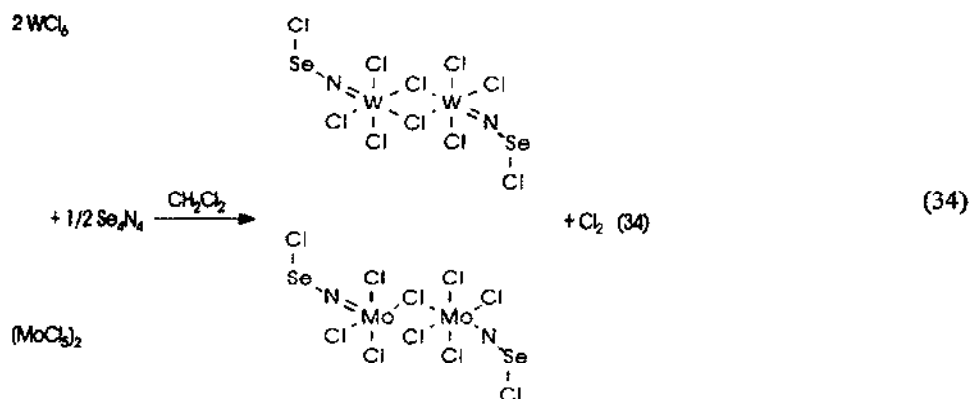
The proposed structure of the resulting air-sensitive diamagnetic non-explosive products is based on an infrared spectroscopic comparison with the analogous well-known chlorothionitrene complexes $[Cl_4M(NSCl)]_2$ with M = W [65] and Mo [66]. Reaction of "Se_4N_2" with WCl_6 gave new access to the tungsten complex $[WCl_4(NSeCl)]_2$ in 90% yield [67]. In 1989, the first binary selenium–nitrogen cations $[Se_3N_2]_2^{2+}$ and $Se_3N_2^{2+}$ were prepared by reacting Se_4N_4 with AsF_5 or Se_4^{2+}. For details, see Section C(i)(b)(II).

(11) Tetraselenium dinitride, Se_4N_2. In 1990, the search for other selenium nitrides beside Se_4N_4 was successful. It was possible to prepare the selenium analogue of S_4N_2 [68], Se_4N_2, by treatment of Se_2Cl_2 with Me_3SiN_3 in 92% yield according to eqn. (35).

$$2\ Se_2Cl_2 + 4\ Me_3SiN_3 \xrightarrow{\ CH_2Cl_2\ } Se_4N_2 + 5\ N_2 + 4\ Me_3SiCl \qquad (35)$$

Tetraselenium dinitride was isolated as a black crystalline powder which is air-sensitive but easy to handle at 22°C. Explosions only occur on heating to 80°C or strong mechanical shock [69]. Its behaviour can be compared to that of S_4N_2 [70]. On the bases of ab initio calculations, the structure and the energies of the fundamental vibration modes have been determined. The values obtained are in excellent agreement with the experimentally observed absorptions in the infrared spectrum, predicting a chair conformation with C_s symmetry and two pairs of different Se–N-bond distances (~1.68 Å and 1.82 Å) for the six-membered ring [69]. Recently, the complexes $[SnCl_4(Se_4N_2)_2]$ and $[TiCl_4(Se_4N_2)]$ have been prepared by reacting Se_4N_2 with $SnCl_4$ or $TiCl_4$ in CH_2Cl_2 according to eqns. (36) and (37).

(36)



(37)
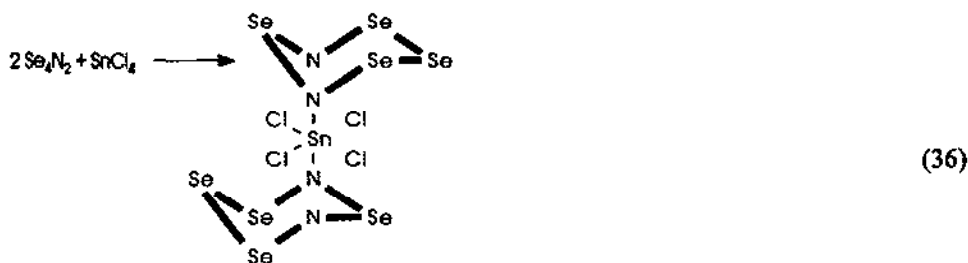
These complexes form red-brown moisture sensitive crystalline powders, which are insoluble in common organic solvents. $[SnCl_4(Se_4N_2)_2]$ contains CH_2Cl_2, which can be extracted with *n*-hexane. Pure dried powder of $[TiCl_4(Se_4N_2)]$ is surprisingly explosive. According to the infrared spectra of the tin complex, both Se_4N_2 units are bonded with one of the nitrogen atoms at the tin atom in *trans* position, whereas in the case of the titanium complex, it is assumed that both nitrogens are bonded in a chelating fashion at the titanium atom as shown above. The ^{119}Sn Mössbauer spectrum of the tin complex also supports the proposed *trans* connection [71]. A re-examination of the reaction between $(CH_3)_3SiN_3$ and Se_2Cl_2 (see eqn. (35)) by Chivers et al. proved the formation of the black solid as described in [69] with an identical IR spectrum but they elucidated a different composition ($Se_3N_2Cl_2$) and structure [72].
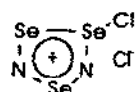
(III) Triselenadiazolium radical, 2,5-di(^{t}Bu)-1,3,4,2,5-triselenadiazolidin, 4,8-di(^{t}Bu)-1,2,3,5,6,7,4,8-hexaselenadiazolin and 3,5,8,10,13,15-hexa(^{t}Bu)-1,2,4,6,7,9,11,12,14-nonaselena-3,5,8,10,13,15-hexazacyclopentadecan. The five-membered ring $[(CH_3)_3C]_2N_2Se_3$ can be prepared by decomposing the unstable selenium diimine $(CH_3)_3C–N=Se=N–C(CH_3)_3$ according to eqn (38).

$$(38)$$

The compound forms yellow needles (m.p. 166°C) and its molecular structure is based on elemental analysis, ^1H, ^{13}C NMR and infrared spectroscopic and mass spectrometric studies [73]. The eight- and fifteen-membered selenium–nitrogen rings (^{t}Bu)$_2$N$_2$Se$_6$ and (^{t}Bu)$_6$N$_6$Se$_9$ are prepared according to eqn. (39).

$$(39)$$
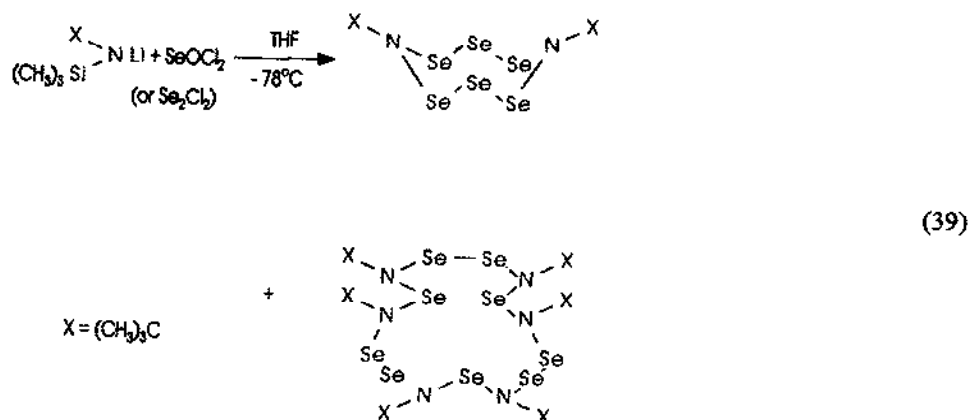
Both compounds are thermally stable and form red-orange crystals (m.p. 169°C) or brown plates (m.p. 153°C), respectively. They are non-explosive, slightly soluble in common organic solvents and have been characterized by mass spectrometry, vibrational and ^1H NMR spectroscopy and X-ray crystallography [74]. Structures are given in Fig. 22.

(IV) 1,1,3,3,5,5-Hexaoxo-1,3,6-triselena-2,4,6-triazolylium cation [M$_3$[(O$_2$)SeN]$_3$ (M = K, NH$_4$, Ag, Tl). Ammonolysis of SeO_2F_2 or $(CH_3O)_2SeO_2$ yields a mixture of Se–N containing compounds from which [NH$_4$]$_3$[(O$_2$)SeN]$_3$ can be isolated [75–78]. The ammonium salt was converted to K$_3$[(O$_2$)SeN]$_3$ by reaction with CH$_3$C(O)OK [75,76,79]. Analogously Ag$_3$[(O$_2$)SeN]$_3$ and Tl$_3$[(O$_2$)SeN]$_3$ were synthesized by metathetical reactions [75]. All salts are highly explosive. In the case of K$_3$[SeO$_2$N]$_3$, the structure of the
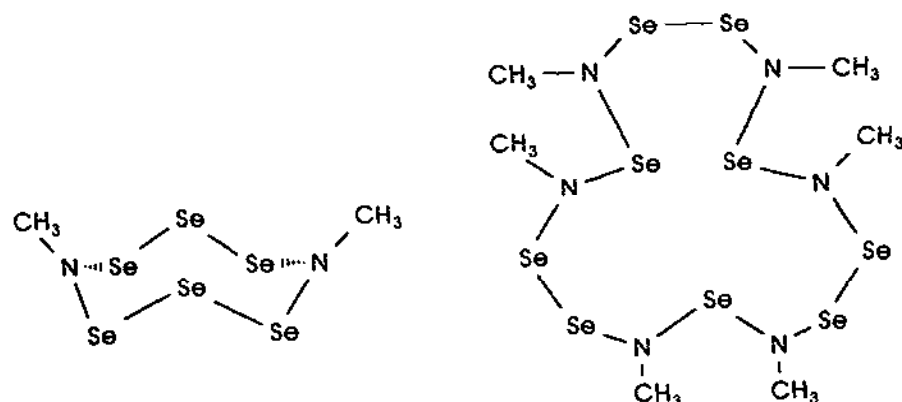
Fig. 22. Crystal structure of $X_2N_2Se_6$ and $X_6N_6Se_9$; X = $(CH_3)_3C$.

anion has been determined by X-ray crystallography. According to Fig. 23, the anion consists of a six-membered ring with a chair conformation. The Se–N distances range from 1.749 to 1.785 Å with a mean value of 1.768(11) Å revealing partial double bond character. Interatomic Se–O distances are in the range of 1.602–1.639 Å with a mean value of 1.622(8) Å [79].

(b) Ternary chalcogen–nitrogen heterocycles

In 1961, Gracia-Fernandez reported the first Se–N–S heterocycle. He treated diselenium dichloride with tetrasulfur tetranitride in thionyl chloride and obtained a colourless solid material which, after washing with carbon tetrachloride, analyzed as $SeS_2N_2Cl_5$. On the basis of its X-ray powder pattern and additional investigations, the ring structure shown in Fig. 24(a) was suggested involving an odd electron [80].

This reaction was re-investigated in 1967 and it was found that the mixture consisted of thiotrithiazyl chloride and a yellow compound (m.p. 85.5°C) which on recrystallization from formic acid was analyzed to give the empirical formula $SeS_2N_2Cl_2$. On the

Fig. 23. Structure of $[(O_2)SeN]_3^{3-}$ in $K_3[(O_2)SeN]_3$.

Fig. 24. Suggested structures for (a) $SeS_2N_2Cl_5$ and (b) $[SeS_3N_3]_2^+ [SeCl_6]^{2-}$

basis of its IR spectrum, which is similar to $[S_4N_3]^+Cl^-$, the structure presented in Fig. 24(b) was suggested. IR: 1171vs, 1008vs, 951vs, 722w, 683s, 667sh, 578w, 562s, 555sh, 463s, 330m, 281w, 254w, 247w, 227w, 212m cm^{-1} [81]. Finally, in 1989, Stammler 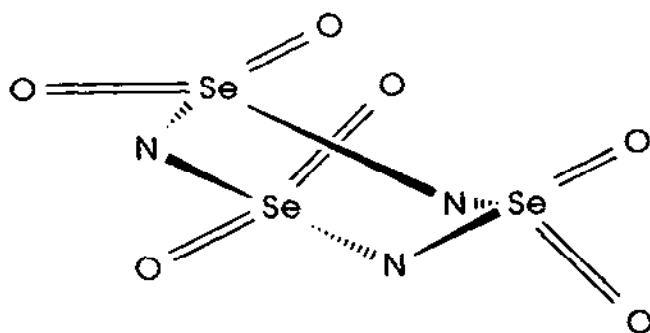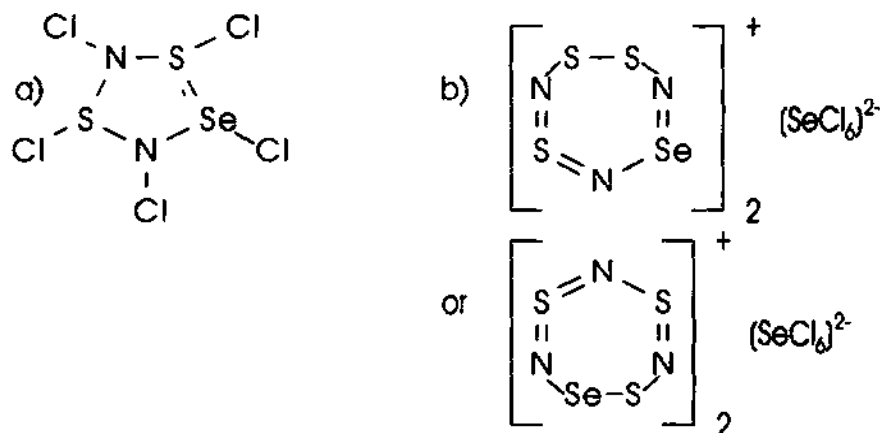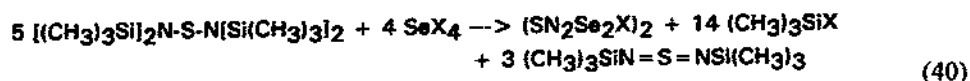and Weiss repeated the reaction and isolated three crystalline products: $[S_4N_3^+]_2[Se_2Cl_{10}]_2$, $[S_4N_3^+]_2[Se_2Cl_6]^{2-}$ and $[S_4N_3]^+[SeCl_5]^-$. X-Ray diffraction studies on the three compounds indicated that Se–N–S heterocycles are not formed. All compounds consisted of ionic moieties containing $[S_4N_3]^+$ with the anions $[Se_2Cl_{10}]^{2-}$, $[Se_2Cl_6]^{2-}$ and $[SeCl_5]^-$. The latter is bridged by one chlorine atom and is therefore polymeric [82].

(1) Cyclothiaselenazenium cations. The first Se–N–S containing ring was synthesized in almost quantitative yield in 1978 by reacting $[(CH_3)_3Si]_2N$–S–$N[Si(CH_3)_3]_2$ with either $SeCl_4$ or $SeBr_4$ in CH_2Cl_2 at 20°C (20 h) according to eqn (40).

$$5 \ [(CH_3)_3Si]_2N\text{-}S\text{-}N[Si(CH_3)_3]_2 + 4 \ SeX_4 \longrightarrow (SN_2Se_2X)_2 + 14 \ (CH_3)_3SiX$$
$$+ \ 3 \ (CH_3)_3SiN=S=NSi(CH_3)_3 \tag{40}$$

$$X = Cl, Br$$

Both materials are dark purple, highly insoluble crystalline powders with a high thermal stability. The chloride decomposes without melting at 175°C and the bromide at 200°C. The molecular structures were elucidated from ESR, IR and mass spectrometric data: $(SN_2Se_2Cl)_2$ IR (Raman): 972s (972vw), 941s (945w), 801w (–), 720w (–), 617vs (618w), 588m (657vw?), 472w (471w), (463m), 356vs (354w), – (258s), – (195w), – (110vs) cm^{-1}. $(SN_2Se_2Br)_2$ IR: 975s, 941s, 720w, 618vs, 585m, 475w, 355vs cm^{-1}.

The two solids show no ESR signal and mass spectra are not published. Their molecular structures are presented in Fig. 25. The decomposition products dissolve in sulfuric or chlorosulfonic acid yielding green solutions [83].
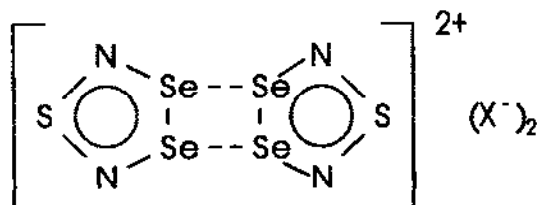
Fig. 25. Molecular structure of $(SN_2Se_2Cl)_2$.

The first unambiguously characterized compounds involving a sulfur-selenium-nitrogen cation ring were $[Se_4S_2N_4]^{2+}[AsF_6^-]_2$ and $[Se_4S_2N_4]_2^+[SbF_6^-]_2$. The blue green crystals of both compounds are obtained in SO_2 by oxidation of S_4N_4 using either Se_4^{2+} or Se_8^{2+} [84] according to eqn. (41).

$$S_4N_4 \quad \begin{array}{l} + \; [Se_4^{2+}][AsF_6^-]_2 \; \text{or} \; [Se_8^{2+}][AsF_6^-]_2 \\ \\ + \; [Se_4^{2+}][Sb_2F_{11}^-]_2 \end{array} \quad \xrightarrow{\quad\quad} \quad \begin{array}{l} [Se_4S_2N_4]^{2+}(AsF_6^-)_2 \\ \\ [Se_4S_2N_4]^{2+}(SbF_6^-)_2 \end{array} \quad (41)$$
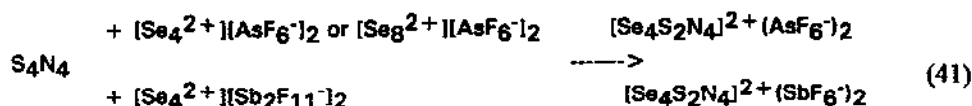
Another route to the dication is the reduction of purified $\overline{[SeNSNSe]}(AsF_6)_2$ (see

Section C(i)(b)(II)) with CsN_3 in SO_2 yielding $[\overline{SeNSNSe}]_2(AsF_6)_2$ quantitatively [93]. With the synthesis of $Se(NSO)_2$ [21,85,86], a new chapter on Se–N–S cationic rings was opened. Bis(sulfinylamino)selane reacts with Lewis acids such as MF_5 (M = As, Sb, Nb) and BF_3, as well as the protic acids $HOSO_2F$ and CF_3SO_2OH; to form bis(1,3,4,2,5-thiadiselenadiazolium) cations with the counter anions AsF_6^-, SbF_6^-, NbF_6^-, BF_4^- [11], OSO_2F^- and $CF_3SO_3^-$ [9]. The structures of the AsF_6^-, SbF_6^- [33]and $CF_3SO_3^-$ [9] salts
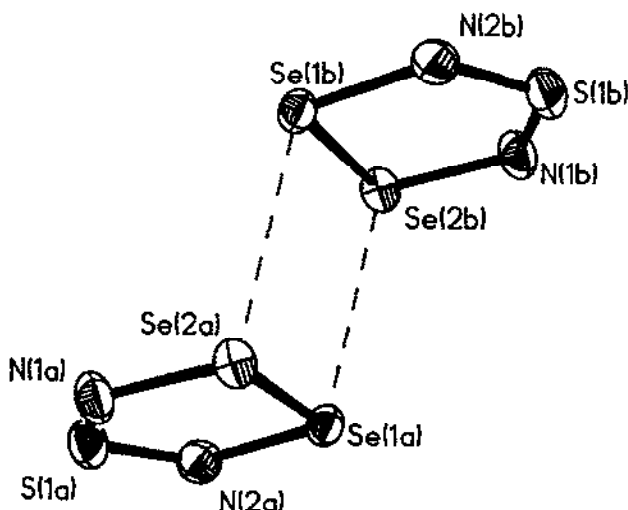
Fig. 26. ORTEP view for $[Se_4S_2N_4]^{2+}$.

TABLE 3

Bond distances (Å) and bond angles (°) for $[Se_2N_2S]^{2+}[X^-]_2$; $X = AsF_6^-$, SbF_6^- and $CF_3SO_3^-$

X	AsF_6^- [84]	SbF_6^- [84]	$CF_3SO_3^-$ [9]
Se(1a)–Se(2a)	2.345(2)	2.356(2)	2.363(1)
Se(1b)–Se(2b)	2.358(2)	2.369(2)	2.363(1)
Se(1a)–N(2a)	1.756(12)	1.771(13)	1.786(4)
Se(2a)–N(1a)	1.755(12)	1.770(13)	1.789(4)
Se(1b)–N(2b)	1.753(12)	1.781(12)	1.786(4)
Se(2b)–N(1b)	1.746(12)	1.756(12)	1.789(4)
Se(2a)–Se(1a)–N(2a)	94.6(4)	93.5(4)	93.2(1)
Se(1a)–Se(2a)–N(1a)	93.2(3)	93.9(4)	93.8(1)
N(1a)–S(1a)–N(2a)	112.0(6)	112.7(7)	113.2(2)
Se(1a)–N(2a)–S(1a)	118.9(6)	120.0(7)	119.5(3)
Se(2a)–N(1a)–S(1a)	121.3(7)	119.9(7)	119.6(3)
Se(2b)–Se(1b)–N(2b)	93.6(4)	92.9(4)	93.8(1)
Se(1b)–Se(2b)–N(1b)	93.6(3)	94.0(4)	93.8(1)
N(1b)–S(1b)–N(2b)	111.6(6)	112.5(7)	113.2(2)
Se(1b)–N(2b)–S(1b)	120.2(6)	120.3(7)	119.5(3)
Se(2b)–N(1b)–S(1b)	120.9(7)	120.3(7)	119.6(3)

were obtained by X-ray crystallographic studies and there is no doubt that they are identical for the other compounds. An ORTEP view of $[Se_4S_2N_4]_2^+$ is provided in Fig. 26 and bond distances as well as bond angles are given in Table 3.

Since the preparation of $[Se_4S_2N_4]_2^+$ via $Se(NSO)_2$ provides the dication in good yields (40–60%), high purity and on a gram scale, it was possible to study their chemistry for the first time. According to Scheme 1 (see Section B(i)(b)) $[Se_4S_2N_4]_2^+$ $[MF_6^-]_2$
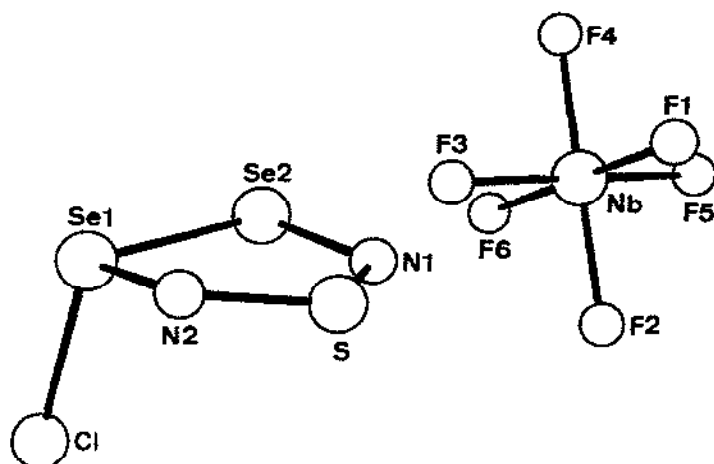
Fig. 27. Crystal structure of $[ClSe_2SN_2]^+[NbF_6]^-$.

(M = As, Sb, Nb) reacts with chlorine and bromine to give 3-halogeno-1,3,4,2,5-thiadiselenadiazolium cations with the corresponding anions. The structure of these cations were determined by X-ray crystallographic methods.

The crystal structure of $[ClSe_2SN_2]^+[NbF_6]^-$ is shown in Fig. 27. It was not possible to synthesize the corresponding fluorine and iodine derivatives.

Another route to the 3-chlorothiadiselenadiazolium cations is the reaction of $Se(NSO)_2$ and $SbCl_5$ (molar ratio 3:2) in CH_2Cl_2 at 22°C providing orange $[ClSe_2SN_2]^+[SbCl_6]^-$. Treatment of $Se(NSO)_2$ with PCl_5 or $SeCl_4$ under analogous conditions gives $[ClSe_2SN_2]^+[Cl^-]$. A slightly different product is obtained when $Se(NSO)_2$ is treated with $POCl_3$ at 50°C for 5 days. The compound formed is isomeric to $[ClSe_2SN_2]^+Cl^-$ and is probably the covalent species $Cl_2Se_2N_2S$. Crystal structures and molecule parameters of $[ClSe_2N_2S][SbCl_6]$, $[ClSe_2N_2S][Cl]$ and $Cl_2Se_2N_2S$ are given in Fig. 28 and Table 4, respectively. $[ClSe_2N_2S]Cl$ is also obtained from chlorination of $(SN_2Se_2Cl)_2$ [11]. If this procedure is carried out in a molar ratio of 1:1 in SO_2 only 50% of the starting material reacts and excess chlorine (20%) had no effect on the reaction. The formation of $[ClSe_2N_2S][Cl]$ was indicated by IR spectroscopy. However, the results provide additional evidence that $(SN_2Se_2Cl)_2$ has a structure similar to the one shown in Fig. 5.

The assumption that $Cl_2Se_2N_2S$ exists in two isomeric forms (ionic and covalent) is based on the fact that although their chemical and physical properties are in general similar, they differ significantly in their IR spectra and crystal data (see Tables 4 and 5) [11].

The literature provides an impressive analogy to this ionic-covalent isomerism. Single crystals have been isolated from the reaction of $S_3N_3Cl_3$ and Se_2Cl_2 which,
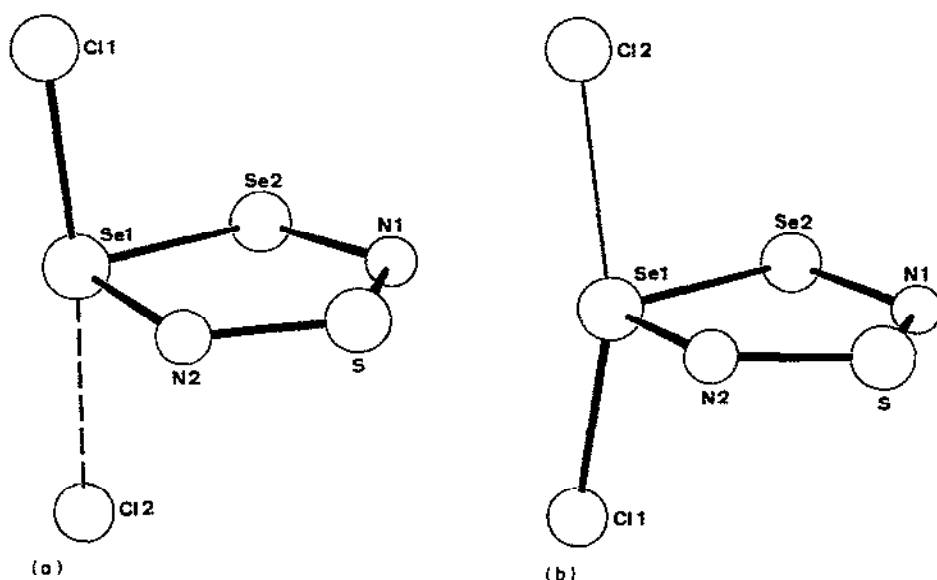

Fig. 28. Structure of $[ClSe_2N_2S]^+[Cl]^-$ and $Cl_2Se_2N_2S$ covalent.

TABLE 4

Bond distances (Å) and bond angles (°) for $[ClSe_2N_2S]^+[Y]^-$; Y = $[NbF_6]^-$, $[SbCl_6]^-$, $[Cl]^-$ and Cl covalent

X	$[NbF_6]^-$	$[SbCl_6]^-$	$[Cl]^-$	Cl-covalent
Se1–Se2	2.377(2)	2.359(2)	2.415(1)	2.384(2)
Se1–N2	1.760(9)	2.02(2)	1.813(3)	1.771(9)
Se1–Cl1	2.211(3)	2.188(3)	2.265(1)	2.351(3)
Se2–N1	1.77(1)	1.80(2)	1.820(2)	1.78(1)
S–N1	1.53(1)	1.49(2)	1.545(3)	1.54(1)
S–N2	1.594(9)	1.46(2)	1.578(3)	1.584(9)
Se1–Cl2	–	–	2.825(1)	2.644(3)
Cl1–Se1–N2	102.6(3)	115.1(5)	–	95.6(3)
Cl1–Se1–Se2	101.9(1)	106.1(1)	98.8(1)	
Cl2–Se1–Cl1	–	–	174.3(1)	164.9(1)
Cl2–Se1–N2	–	–	87.6(1)	–
Cl2–Se1–Se2	–	–		92.5(1)
N2–Se1–Se2	94.1(3)	81.1(4)	94.9(1)	94.4(3)
N1–Se2–Se1	92.4(3)	93.6(5)	91.7(1)	93.0(3)
N2–S–N1	111.9(5)	107.6(9)	114.8(1)	113.5(5)
S–N1–Se2	121.7(6)	120(1)	120.8(2)	120.3(6)
S–N2–Se1	118.8(5)	113.4(9)	117.2(2)	118.6(5)

according to the X-ray crystal structure, contain two molecules with the following structures in the unit cell. For the covalent moiety d(Se–Cl) = 2.433(3) and 2.475(2) Å and for the ionic form d(Se–Cl) = 2.249(3) and 2.917 (2) Å [87]. Although the values are significantly different, it cannot be said without reservation that this is entirely due to ionic-covalent isomerism. For example, crystal packing effects may also cause such deviations.

    Additional evidence for the formation of an ⌐‾‾⌐ $[ClSeNSNS]^+$ cation is provided by reaction of RSeCl (R = C_2H_5, n-C_4H_5) with $[NS]^+[AlCl_4]^-$ in CH_2Cl_2 at −78°C. On warming to 23°C, ⌐‾⌐ $[ClSeNSNS][AlCl_4]$ was isolated and the structure was determined by X-ray crystallography (Fig. 29). Selected bond distances and angles are presented in Table 6. The SeS_2N_2 ring is almost planar with the chlorine atom bonded to selenium. The bond distance d(Se–Cl) = 2.191(1) Å is 0.058 Å shorter than that in ⌐‾‾⌐ $[ClSeNSNSe]^+Cl$ and confirms the ionic structure of this ⌐‾⌐ $Cl_2SeNSNS$ moiety [88].

    Reactions between Se(NSO)$_2$ and Lewis acids or protic acids described so far exhibit the transformation of a non-cyclic molecule into a five-membered heterocycle and deserves comment. According to Scheme 1 (see Section B(i)(b)), it can be assumed that in the first step Se(NSO)$_2$ undergoes an intramolecular condensation forming SO$_2$ and ⌐‾⌐ the four-membered ring SeNSN. It is known that S_2N_2 dimerizes in solution to S_4N_4

TABLE 5

IR absorptions and tentative assignments for $[ClSe_2N_2S]^+[Z]^-$; Z = Cl covalent, $[Cl]^-$, $[SbCl_6^-]$, $[AsF_6]^-$, $[NbF_6]^-$ and $[BrSe_2N_2S]^+[AsF_6]^-$

$Cl_2Se_2N_2S$ (covalent)	$[Cl]^-$	$[SbCl_6]^-$	$[AsF_6]^-$	$[NbF_6]^-$	$[BrSe_2N_2S]$ $[AsF_6]$	
1012m	1017m	1016m	1025m	1029m	1022m	ν_{as} (NSN)
908s	915s	929s	922s	927s	919s	ν_s (NSN)
			698vs		698vs	
			676s	688m	674s	ν_3 (MF$_6$)
		635m	636m		637w	
612s	612s	619s	623s	627vs	620s	ν(Se–N)
607m	591m		562m	566m	562w	
600m				533s		
476w		490w	495w			
473w	464w					δ (NSN)

[89,90] and it is only reasonable to assume that $\overline{\text{SeNSN}}$ behaves similarly to form $Se_2S_2N_4$ with an S_4N_4-like cage structure and a Se–Se bond. In this cage, the five-membered heterocycle is preformed and only requires loss of N_2S. Support for this pathway is provided by the fact that in all reactions in which $Se(NSO)_2$ is involved SO_2 and nitrogen are the main volatile products, as well as sulfur in the residue. Additional support can be drawn from the reaction between $Se(NSO)_2$ and $TiCl_4$ in CH_2Cl_2. Here the only volatile product is SO_2 and an orange-yellow coloured solid precipitates [11] according to Scheme 1 (see Section B(i)(b)). In agreement with $S_2N_2 \cdot TiCl_4$, formed from S_4N_4 and $TiCl_4$ [91], $SeSN_2 \cdot TiCl_4$ is insoluble in SO_2, $CHCl_3$, CH_2Cl_2, SO_2ClF, $SOCl_2$, $POCl_3$ and toluene. It exhibits a comparable colour, thermal stability and similar IR spectrum. An X-ray powder analysis showed both molecules to be isostructural.

A more soluble derivative was obtained by reaction with AsF_5, giving bright yellow crystals with the stoichiometrical composition $SeS_3N_5AsF_6$. X-Ray structure analysis indicated a structure similar to $[S_4N_5]^+$, and its IR spectrum was similar to that of
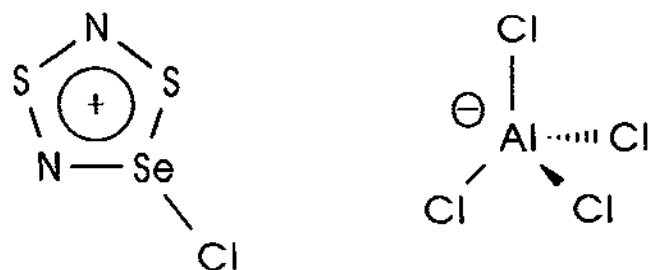

Fig. 29. Structure of $ClSeNSNS^+AlCl_4^-$.

TABLE 6

Selected bond distances (Å) and bond angles (°) of $\overline{CISeNSNS}^{+}AlCl_4^{-}$

Se1–S1	2.293(1)	S1–Se1–Cl5	101.46(5)
S1–N1	1.630(4)	S1–Se1–N2	92.7(1)
N1–S2	1.545(4)	Cl5–Se1–N1	103.7(1)
S2–N2	1.578(4)	Se1–S1–N1	96.1(1)
N2–Se1	1.741(4)	N1–S2–N2	110.2(2)
Se1–Cl5	2.191(1)	S1–N1–S2	121.6(2)
		Se1–N2–S2	118.6(2)

$[S_4N_5]^{+}[AsF_6]^{-}$ [92]. The crystal structure exhibits double occupation of the general positions of the asymmetric unit. Comparable but slightly distorted geometries of the two independent AsF_6^{-} anions give significant differences for opposite Se–N bond distances in the skeleton of the cations. The crystal structure for molecule A is given in Fig. 30. Selected parameters for both molecules are presented in Table 7. For IR and Raman data, see the original paper [11].

(II) Thiadiselena-, triselenadiazolium cations and radical cations. Several methods have been described for the preparation of 1,3,4,2,5-thiadiselenadiazolium-bis-

(hexafluoroarsenate). It is formed in good yields by oxidizing $\overline{(SeNSNSe)}_2(AsF6)_2$ with excess AsF_5 in SO_2 solution [11,93], by reacting $Se_4(AsF_6)_2$ with S_4N_4 in SO_2 at 20°C (12 h) [93] and from reaction of Se(NSO)_2 with a threefold excess of AsF_5. Metathesis of $[\overline{CISeNSNSe}](AsF_6)$ with Ag[AsF_6] in SO_2 at 22°C (24 h) gave 90% yield [11]. The X-ray crystal structure consists of discrete planar $\overline{(SeNSNSe)}^{2+}$ and AsF_6^{-} with significant cation–anion interactions (Fig. 31(a)) [93]. The colourless crystals (m.p. 197°C) are soluble in SO_2 and stable for weeks at 22°C but they are very sensitive to moist air. ^{77}Se NMR investigation in SO_2 exhibits one peak extremely shifted to low field at δ 2435 [11]
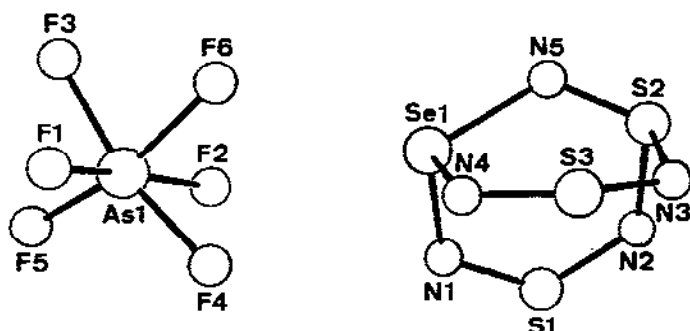
Fig. 30. Crystal structure of $[SeS_3N_5]^{+}[AsF_6]^{-}$.

TABLE 7

Selected parameters for molecules A and B in (Å) and (°), respectively

	A	B
Se1–N1	1.75(2)	1.95(2)
Se1–N4	1.85(2)	1.81(2)
Se1–N5	1.90(2)	1.70(1)
S1–N1	1.54(2)	1.49(2)
S1–N2	1.59(2)	1.51(2)
S2–N2	1.73(2)	1.76(2)
S2–N3	1.78(2)	1.69(2)
S2–N5	1.47(2)	1.68(2)
S3–N3	1.52(2)	1.54(2)
S3–N4	1.50(2)	1.54(2)
N4–Se1–N1	100.3(7)	97.5(7)
N2–S1–N1	118.7(9)	124(1)
N3–S2–N2	96.9(8)	92.5(8)
N4–S3–N3	124(1)	118.4(9)
S2–N5–Se1	122(1)	115.9(8)

or δ 2412 [93] (external standard CH_3SeCH_3) indicating that the two Se atoms are magnetically equivalent. For IR and Raman spectra, see [11,93]. When a 3:1 or 5:1 excess of XSO_3H (H = F, CF_3) is reacted with $Se(NSO)_2$ in SO_2, it is possible to detect the dication by ^{77}Se NMR spectroscopy in addition to a signal at δ 1600. However, on removal of the solvent, only $[\overline{SeNSNSe}]_2[XSO_3]_2$ can be isolated [9]. According to an ESR spectroscopic investigation and magnetic measurements, $[\overline{SeNSNSe}]_2[AsF_6]_2$ exhibits no radical character in the solid state. However, in SO_2 solution, the radical cation

Fig. 31. (a) Structure of the $SeNSNSe^{2+}$ cation. (b) The structure of the two crystallographically unique centrosymmetric $[Se_3N_2^{+\cdot}]_2$ dimers. (c) Structure of $[Se_3N_2]^{2+}$.

TABLE 8

g and hyperfine tensors for selenathiadiazolylium radicals in SO_2 and D_2SO_4 matrices at 77 K

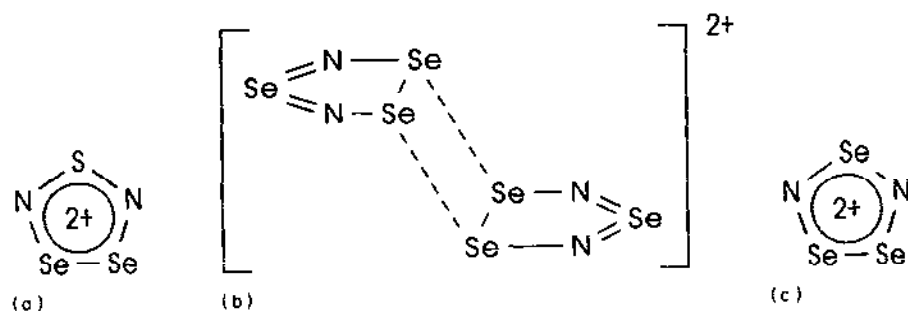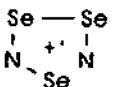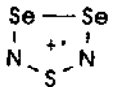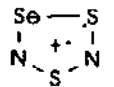|	Se — Se N $\overset{+\cdot}{\underset{Se}{}}$ N		Se — Se N $\overset{+\cdot}{\underset{S}{}}$ N		Se — S N $\overset{+\cdot}{\underset{S}{}}$ N	
Solvent	SO_2	D_2SO_4	SO_2	D_2SO_4	SO_2	D_2SO_4
g_{xx}	1.9930	n.m.[d]	1.9941	1.9931	1.9957	1.9953
$a_{xx}(2^{14}N)$[a]	7.44	n.m.	6.92	7.28	8.33	8.00
$a_{xx}(^{77}Se)$[b]	180	n.m.	180	180	198	200
g_{yy}	2.0108	n.m.	2.0108	2.0124	2.0086	2.0096
$a_{yy}(2^{14}N)$[a]	~0	n.m.	~0	~0	~0	~0
$a_{yy}(^{77}Se)$[b]	70	n.m.	70	70	78	n.m.
g_{zz}	2.1379	2.1408	2.1355	2.1369	2.0736	2.0734
$a_{zz}(2^{14}N)$[a]	~0	~0	~0	~0	~0	~0
$a_{zz}(^{77}Se)$[b]	43	n.m.	45	50	75	74
$\langle g \rangle$	2.0472	–	2.0468	2.0475	2.0260	2.0261
g_{iso}	2.0464	–	2.0464	2.0472	2.0255	2.0262
p–p width[c]	34	–	34	22	15	12

[a]Values in gauss.
[b]Hyperfine coupling, in gauss, ascribed to ^{77}Se at the 1,2 positions.
[c]Maximum slope linewidth, in gauss, of isotropic spectrum.
[d]Not measured because feature to weak or obscured.

[SeNSNSe]$^{+\cdot}$ is detectable. The ESR spectrum shows a quintet with a coupling constant of 3.06 G indicating the equivalency of the two nitrogen atoms [11].

Electron spin resonance investigation on dilute solutions of hexafluoroarsenate salts of selenathiadiazolylium cations (obtained either by reacting $Se_4(AsF_6)_2$ with S_4N_4 in SO_2 solution and oxidizing the product formed with excess AsF_5 in the presence of traces of bromine, or by treating $Se_8(AsF_6)_2$ with 4 equiv. of $NS(AsF_6)$ in SO_2 solution; the black crystals formed were selected by hand and redissolved in SO_2 for ESR measurements) proved the existence of three selenathiadiazolium radicals which are presented with their g and hyperfine tensors in Table 8 [94].

The first binary Se–N cations $Se_3N_2^{+\cdot}$ and $Se_3N_2^{2+}$ were prepared in high yield in 1989 by the reaction of stoichiometric quantities of $Se_4(AsF_6)_2$ or AsF_5 with Se_4N_4 in liquid SO_2 according to eqns. (42)–(45).

$$Se_4N_4 + Se_4(AsF_6)_2 \longrightarrow (SeNSeNSe)_2(AsF_6)_2 + 2 Se \qquad (42)$$

$$3 Se_4N_4 + 6 AsF_5 \longrightarrow 2 (SeNSeNSe)_2(AsF_6)_2 + 2 N_2 + 2 AsF_3 \qquad (43)$$

$$3\ Se_4N_4\ +\ 12\ AsF_5\ \xrightarrow{\hspace{1cm}}\ 4\ SeNSeNSe(AsF_6)_2\ +\ 2\ N_2\ +\ 4\ AsF_3 \tag{44}$$

$$(SeNSeNSe)_2(AsF_6)_2\ +\ 3\ AsF_5\ \xrightarrow{\hspace{1cm}}\ 2\ SeNSeNSe(AsF_6)_2\ +\ AsF_3 \tag{45}$$
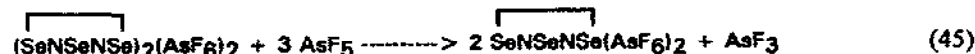
Both cations are stable on grinding, on manipulation with a nickel spatula and on heating. Their identities were confirmed by X-ray crystallographic studies. $(SeNSeNSe)_2(AsF_6)_2$ dimers of the 7π radical cation $Se_3N_2^{+\cdot}$ are weakly linked in a centrosymmetric *trans* arrangement illustrated in Fig. 31(b). The structure of the 6π cation $Se_3N_2^{2+}$ is shown in Fig. 31(c). Although the selenium–selenium distance and the adjacent selenium–nitrogen distances are all shorter in the dication, the Se–N bond distances in both cations, $[Se_3N_2]_2^{2+}$ and $[Se_3N_2]^{2+}$, are indicative of significant π-bonding (for bond distances see Table 9). Raman and ^{14}N NMR spectroscopic studies of $Se_3N_2^{2+}$ in liquid AsF_3 and SO_2, respectively, proved that the ring structure is retained in solution [95].

(III) Metal–selenium–nitrogen heterocycles. The first example of a metal-selenium–nitrogen heterocycle was prepared in 1989. The reaction of Se_4N_4 with $PtCl_2[P(CH_3)_2C_6H_5]_2$ in $CHCl_3$ provided a mixture containing $Pt(Se_3N)Cl[P(CH_3)_3C_6H_5]$ (15) which was characterized by X-ray crystallography to be square planar with a bidentate Se_3N^--ligand (analogous to S_3N^-) coordinated through two selenium atoms. This preparation was the motivation for an extended investigation on Se–N anion chemistry [96].

$$Se_4N_4 + PtCl_2[P(CH_3)_2C_6H_5]_2\ \xrightarrow{CHCl_3}\ [C_6H_5(CH_3)_2\ P]Pt(Cl)(Se_3N) \tag{46}$$

$$\underset{=}{15}$$
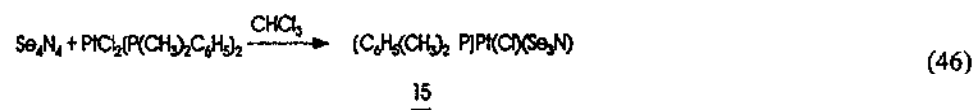
Chromatographic separation of the reaction mixture gave also $[C_6H_5(CH_3)_2PPtCl$

TABLE 9

Bond distances (Å) for $[Se_3N_2]_2^{2+}$ and $[Se_3N_2]^{2+}$; (values in parentheses correspond to the other independent dimer)

$[Se_3N_2]_2^{2+}$		$[Se_3N_2]^{2+}$	
Se1–Se2	2.398(3) (2.395(3))	Se1–Se2	2.334(3)
Se1–N1	1.761(15) (1.739(14))	Se1–N2	1.734(21)
Se3–N1	1.691(15) (1.724(14))	Se3–N2	1.698(21)
Se3–N2	1.688(14) (1.703(14))	Se3–N1	1.689(18)
Se2–N2	1.759(14) (1.769(14))	Se2–N1	1.744(20)
Se1–Se2a	3.123(3) (3.149(3))		
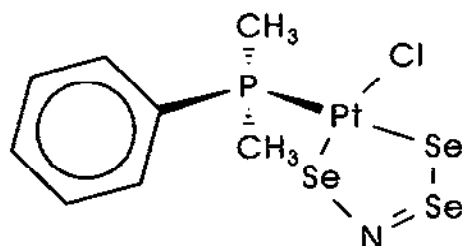
Fig. 32. Crystal structure of **15**.

[Se$_2$N$_2$H]]$^+$, characterized by mass spectrometry and following halogen-phosphinic exchange, this yielded 2% of [[C$_6$H$_5$(CH$_3$)$_2$P]$_2$Pt{Se$_2$N$_2$H]]$^+$Cl$^-$ (**16**) (Fig. 33) [97] according to eqn. (47).

$$(C_6H_5(CH_3)_2P)Pt(Cl)(Se_2N_2H) \xrightarrow{C_6H_5(CH_3)_2P} [(C_6H_5(CH_3)_2P)_2Pt(Se_2N_2H)]^+ Cl^-$$

$$\mathbf{16}$$

(47)
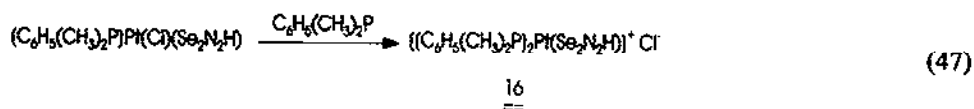
Due to the explosiveness of Se$_4$N$_4$, alternative methods of preparation were investigated. The reaction of SeCl$_4$ with NH$_3$ and Cl$_2$Pt[P(CH$_3$)$_2$C$_6$H$_5$]$_2$ led to [C$_6$H$_5$(CH$_3$)$_2$P]2Pt[Se$_2$N$_2$] (**17**), and protonation with HBF$_4$ gave [[C$_6$H$_5$(CH$_3$)$_2$P]$_2$ Pt[Se$_2$N$_2$H]$^+$BF$_4^-$ (**18**) in 70% yield [97], according to eqn. (48).

$$SeCl_4 + NH_3 + [C_6H_5(CH_3)_2P]_2PtCl_2 \longrightarrow (C_6H_5(CH_3)_2P)_2Pt(Se_2N_2) \xrightarrow{HBF_4} [(C_6H_5(CH_3)_2P)_2Pt(Se_2N_2H)]^+ BF_4^-$$

$$74\% \quad \mathbf{17} \qquad\qquad \mathbf{18}$$

(48)
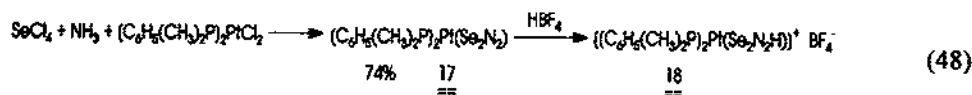
Fig. 33. Structure of **16**.
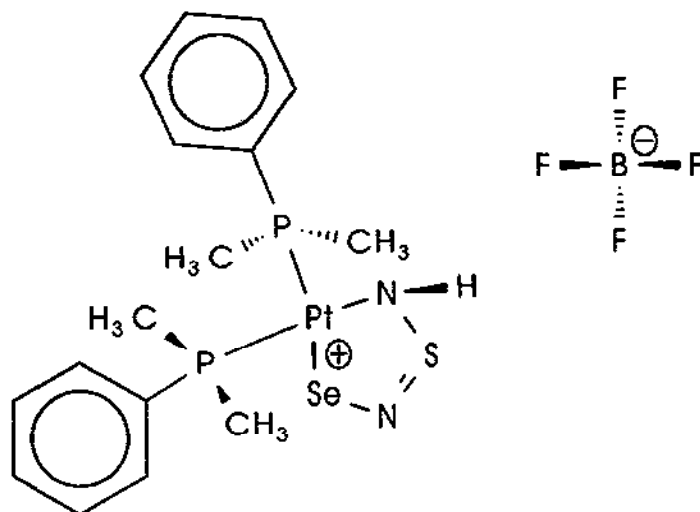
Fig. 34. Structure of 20.

Reaction of $[Se_2SN_2]_2Cl_2$ with $PtCl_2[P(CH_3)_2C_6H_5]_2$ in liquid NH_3 provides $Pt(SeSN_2)[P(CH_3)_2C_6H_5]_2$ (19) which is also protonated with HBF_4 (eqn. (49)). Both compounds, 19 and $[Pt(SeSN_2H)[P(CH_3)_2C_6H_5]_2]^+BF_4^-$ (20) were characterized by IR and ^{31}P NMR spectroscopy as well as by X-ray crystallography [98] (Fig. 34).

(49)
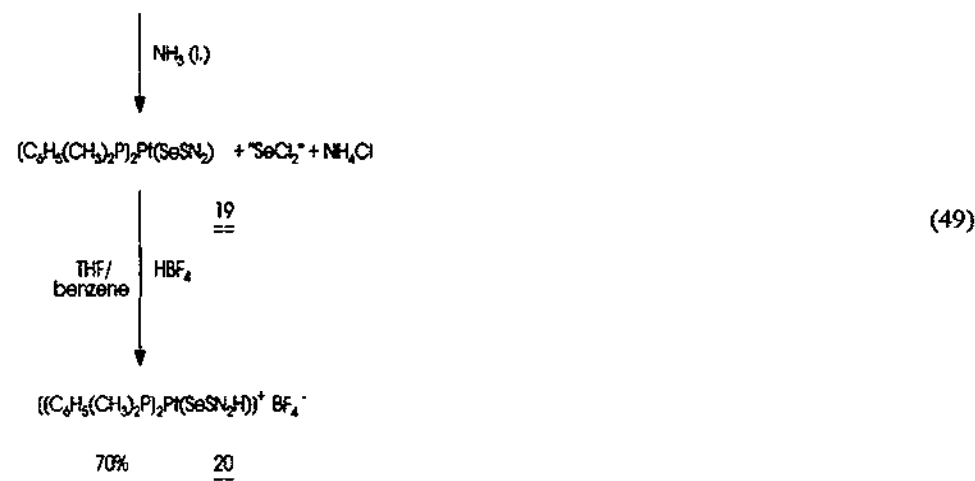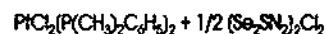
Reaction of the zero valent platinum compound $Pt[P(C_6H_5)_3]_3$ with Se_4N_4 in CH_2Cl_2 leads to a mixture of $Pt(Se_2N_2)[P(C_6H_5)_3]$ (21) and an intermediate species, which decomposes via loss of $(C_6H_5)_3P$ to give $[Pt[Se_2N_2][P(C_6H_5)_3]]_2 \cdot CH_2Cl_2$ (22) (eqn. (50). X-Ray crystallographic studies showed 22 to be dimeric with $[Pt[Se_2N_2][P(C_6H_5)_3]]$ units bridged by
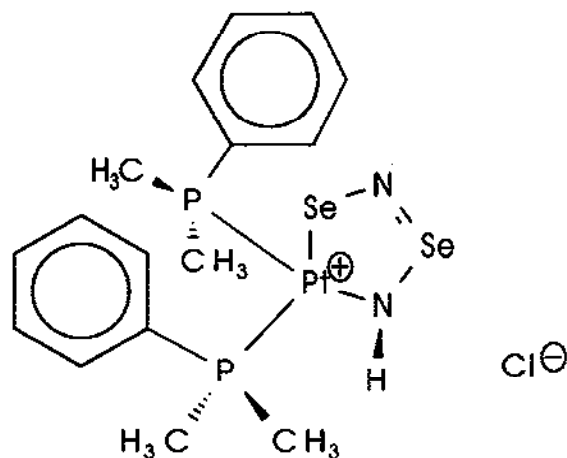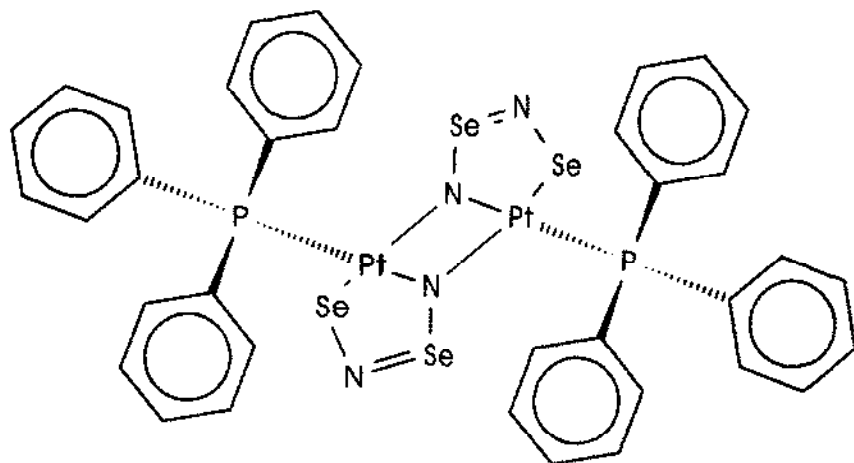
Fig. 35. Structure of **22**.

Pt–N bonds in a Pt_2N_2 ring (Fig. 35). The geometry of the individual $PtSe_2N_2$ rings is comparable to that in **16** [100].

$$Se_4N_4 + Pt(P(C_6H_5)_3) \xrightarrow{\quad CH_2Cl_2 \quad} Pt(Se_2N_2)(P(C_6H_5)_3)_2$$
$$\underset{\text{\underline{\underline{21}}}}{\quad}$$
$$+ Pt_2(Se_2N_2)(P(C_6H_5)_3)_3 \tag{50}$$

$$Pt_2(Se_2N_2)(P(C_6H_5)_3)_3 \xrightarrow[\text{- }P(C_6H_5)_3]{\quad\quad\quad} [((C_6H_5)_3P)Pt(Se_2N_2)]_2$$
$$\underset{\text{\underline{\underline{22}}}}{\quad}$$
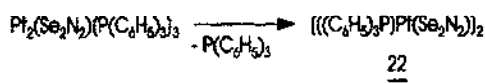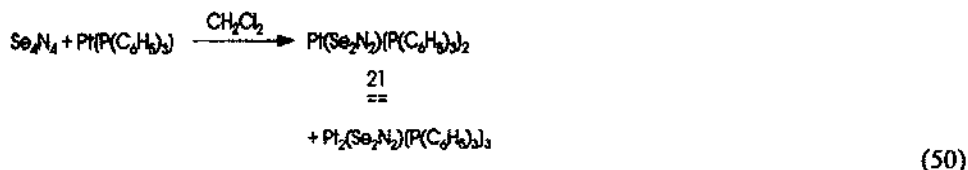
Coordination of unstable chalcogen–nitrogen containing anions such as Se_3N^-, $Se_2N_2H^-$, $Se_2N_2^{2-}$, $SeSN_2^{2-}$ at transition metals is, so far, the only way to stabilize and study such species.

(IV) Selenium–nitrogen heterocycles containing carbon or phosphorus. The research on neutral, low dimensional conducting materials has motivated interest in the preparation of heterocyclic thiazyl radicals [101], especially the 1,2,3,5-dithiadiazolyls $[S_2N_2CR]^\cdot$ [102–106]. Replacement of sulfur by selenium has recently been achieved using the same approach as employed in the preparation of $[S_2N_2CR]^\cdot$.

$$\tag{51}$$
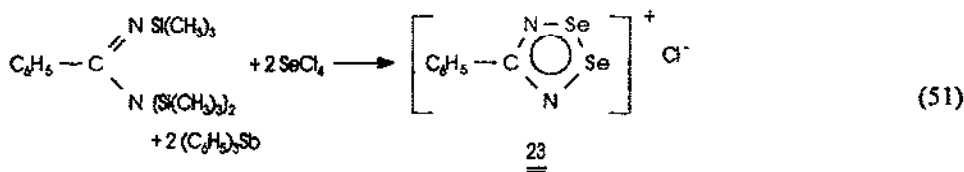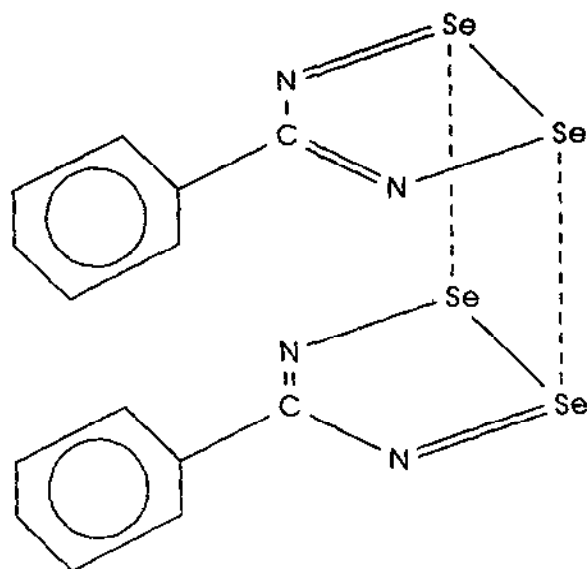
Fig. 36. Structure of **25**.

4-Phenyl-1,2,3,5-diselenadiazoline ring (**23**) can be converted by metathesis with NOPF$_6$ into the corresponding PF$_6^-$ salt, [C$_6$H$_5$CN$_2$Se$_2$]$^+$PF$_6^-$ (**24**), and its structure has been confirmed by X-ray crystallography (see [107]). Like [C$_6$H$_5$CN$_2$S$_2$]$^+$Cl$^-$, **23** can be reduced chemically by (C$_6$H$_5$)$_3$Sb to give the radical dimer [C$_6$H$_5$CN$_2$Se$_2$]$_2$ (**25**). It forms black needles in the solid state (decomposition 178°C), which dissociate partially in CH$_2$Cl$_2$ to the diselenadiazolyl radical [C$_6$H$_5$CN$_2$Se$_2$]$^·$ (ESR (295 K): $g = 2.0394$ (br). Sublimation provided crystals suitable for X-ray crystallographic investigation [107] (Fig. 36).
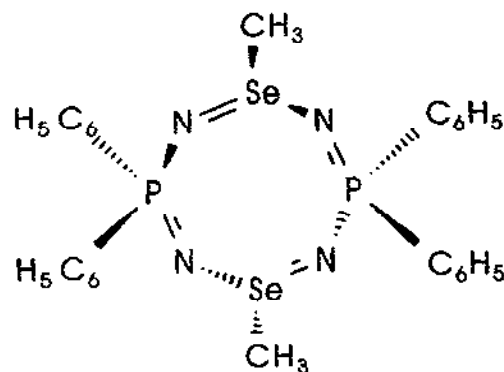
Fig. 37. Structure of 1,5-(C$_6$H$_5$)$_4$P$_2$N$_4$Se$_2$(CH$_3$)$_2$.

In 1989, preparation of the first cyclophosphaselenazenes was reported involving cyclocondensation of $RSeCl_3$ ($R = C_6H_5$, CH_3, C_2H_5) with $(C_6H_5)_2P[NSi(CH_3)_3]$ $[N[Si(CH_3)_3]_2]$. The resulting eight-membered ring, $1,5\text{-}(C_6H_5)_4P_2N_4Se_2(CH_3)_2$ (26) was characterized by X-ray crystallography, showing a chair conformation with the two selenium atoms displaced on either side of the P_2N_4 plane (Fig. 37). When R is equal to CH_3 or C_2H_5, this reaction also produces $1,5\text{-}(C_6H_5)_4P_2N_4Se_2$ (27) and treatment of 27 with $CH_3SO_3CF_3$ in CH_3CN at 0°C gives $1,5\text{-}(C_6H_5)_4\text{-}2\text{-}(CH_3)P_2N_4Se_2$ (28) (eqn. (52)). ^{31}P NMR spectroscopic data of 27 and 28 indicate the presence of a trans-annular Se–Se bond [108].

(52)
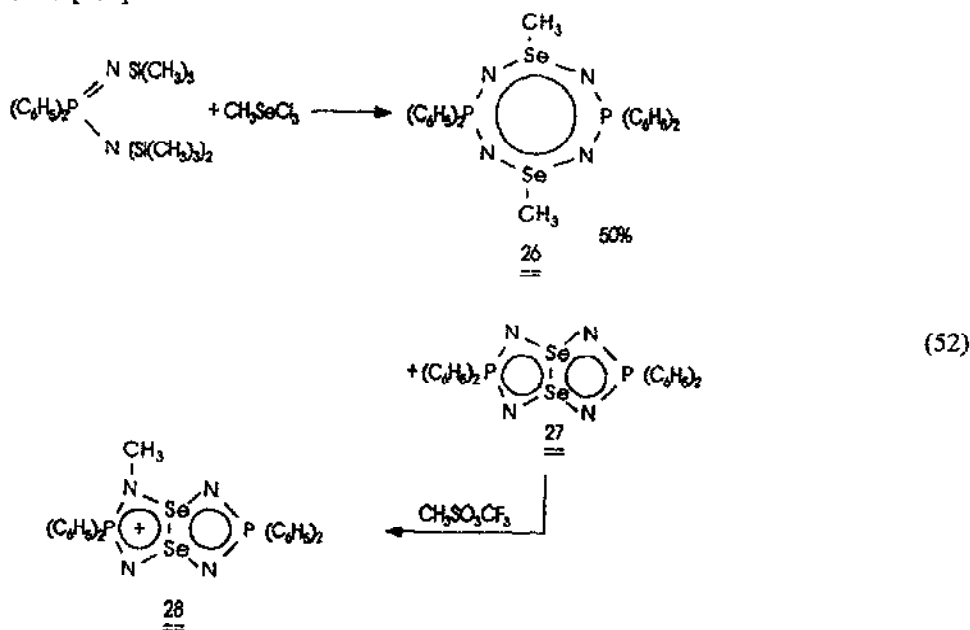
The properties and structures of cyclic Se–N compounds show great similarities to those of binary S–N chemistry. Formation and stability of charged five-membered ring systems are especially remarkable. Such compounds have been intensively investigated and it was found that $Se_3N_2^+$ and $Se_3N_2^{2+}$ contain even Se–N double bonds. Except for $SeSN_2 \cdot TiCl_4$ and Se_4N_2, there are no selenium derivatives of binary S–N rings (4,6,7,8-membered species). Compounds such as $(S_nSe_{4-n}N_3)Cl$, $Se_4N_4^{2+}$, $Se_5N_6^+$ etc. are still unknown.

(ii) Acyclic selenium–nitrogen compounds containing Se–N single bonds

Whereas acyclic sulfur–nitrogen compounds containing S–N single-, double- and triple-bonding are known, Se–N chemistry is restricted to Se–N single- and double-bond systems only. This section gives a survey of these compounds taking into consideration the oxidation state at the selenium atom.

(a) Se^{II}–N compounds

Stable Se^{II}–N compounds were first described in 1963. Reaction of perfluoro-alkylselenylchlorides with dimethylamine gave $CF_3SeN(CH_3)_2$ and $C_3F_7SeN(CH_3)_2$ [109]. The corresponding diamide $[(CH_3)_2N]_2Se$ prepared in 1965, turned out to be unstable at room temperature [110] (eqn. (53)).

$$SeOCl_2 + 4 (CH_3)_2NH \xrightarrow[-2 (CH_3)_2NH_2 + Cl^-]{} [(CH_3)_2N]_2SeO \xrightarrow[-\frac{1}{2}O_2]{} [(CH_3)_2N]_2Se \qquad (53)$$

Increasing stability is observed in polyselanes $[R_2N]_2Se_n$ ($n = 2$–4, R = $(CH_2)_5$, $(CH_2)_4O$. X-Ray structure analysis of these compounds showed that the average Se–N bond length (1.83–1.85 Å) [111–113] corresponds to a Se–N single bond distance (1.86 Å). In 1984, CF_3SeN-derivatives were synthesized [114] (according to eqns. (54)–(57)).

$$CF_3SeCl + (F_3CS)_2NH \xrightarrow[-HCl]{(CH_3)_3N} F_3CSeN(SCF_3)_2 \qquad (54)$$

$$CF_3SeCl + [(CH_3)_3Si]_2NH \longrightarrow [(CH_3)_3Si]_2NSeCF_3 + (CH_3)_3SiN(SeCF_3)_2 \\ 51\% \qquad\qquad\qquad 5\% \qquad (55) \\ + (CH_3)_3SiN(H)SeCF_3 \\ 20\%$$

$$(CF_3Se)_2NH + (CH_3)_3SiCl \xrightarrow[-HCl]{(C_4H_9)_3N} (CH_3)_3SiN(SeCF_3)_2 \qquad (56)$$

$$(F_3CSe)_2NH + S_3N_3Cl_3 \xrightarrow[\substack{Acridin \\ -HCl}]{50°C/CCl_4} F_3C\text{-}Se\text{-}N=S=N\text{-}SeCF_3 \qquad (57)$$

All of these compounds were characterized by NMR (^{19}F, ^{13}C, ^{77}Se) spectroscopy and elemental analysis (Table 10). The tri-substituted $(CF_3Se)_3N$ is accessible by reaction of CF_3SeBr and NH_3 with strict conditions [115] (eqn. (58)).

TABLE 10

Preparation conditions of $(CF_3Se)_nNH_{3-n}$

n	T (°C)	t (h)	CF_3SeBr/NH_3	Yield (%)
3	−10	2–3	3:4	30
2	−20	6	2:3	61
1	0	1	1:3	22.5

$$n \ CF_3SeBr + (n+1)NH_3 \longrightarrow (CF_3Se)_nNH_{3-n} + n \ NH_4Br \tag{58}$$

In 1985, the chloro-analogue of $CF_3SeN[Si(CH_3)_3]_2$ was prepared, according to eqn. (59) characterized by IR and NMR spectroscopy (^1H, ^{13}C, ^{24}Si), mass spectrometry and elemental analysis [73]. The corresponding bromine derivative was isolated from the reaction of $[SeN[Si(CH_3)_3]_2]_2$ with Br_2 in CCl_4 [116]. $[SeN[Si(CH_3)_3]_2]_2$ is formed by reaction of Se_2Cl_2 with $LiN[Si(CH_3)_3]_2$ in $(C_2H_5)_2O$ [86] (eqn. (60)).

$$SeOCl_2 + LiN[Si(CH_3)_3]_2 \longrightarrow ClSeN[Si(CH_3)_3]_2 \tag{59}$$

$$\begin{array}{c} (C_2H_5)_2O \\ 2 \ Se_2Cl_2 + 4 \ LiN[Si(CH_3)_3]_2 \longrightarrow Se[N[Si(CH_3)_3]_2]_2 \\ + \ [SeN[Si(CH_3)_3]_2]_2 + 4 \ LiCl + Se \end{array} \tag{60}$$
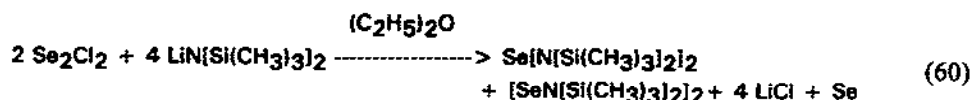
Whereas $BrSeN[Si(CH_3)_3]_2$ and $[SeN[Si(CH_3)_3]_2]_2$ are coloured oils [86,116], $Se[N[Si(CH_3)_3]_2]_2$ is a colourless solid and X-ray structural analysis was performed [117]. ^{77}Se NMR spectroscopic data for these compounds are presented in Table 11.

$(Se(NSO)_2$ was prepared in 1987 and is a very important synthon for development in Se–N chemistry. It is accessible in high yields by reacting Se_2Cl_2 with $(CH_3)_3SiNSO$ in $[(CH_3)_3Si]_2O$ [21] (eqn. (61)).

$$\begin{array}{c} [(CH_3)_3Si]_2O \\ Se_2Cl_2 + 2 \ (CH_3)_3SiNSO \longrightarrow Se(NSO)_2 + Se + 2 \ (CH_3)_3SiCl \end{array} \tag{61}$$

$Se(NSO)_2$ (Fig. 38) is isostructural to $S(NSO)_2$ [22] with an Se–N distance of 1.827 Å. Additional characterization was done by IR and NMR spectroscopy, mass spectrometry and elemental analysis. Other Se^{II} compounds containing the SeNSO group include CF_3SeNSO [118] and $C_6H_2(CF_3)_3SeNSO$ (Fig. 39) [119], which are accessible by the reactions 62 and 63.

$$C_6H_2(CF_3)_3SeCl + (CH_3)_3SiNSO \longrightarrow C_6H_2(CF_3)_3SeNSO + (CH_3)_3SiCl \tag{62}$$

TABLE 11

^{77}Se NMR shifts of $SeN[Si(CH_3)_3]_2$ containing compounds

Compound	δ
$BrSeN[Si(CH_3)_3]_2$	1517
$Se[N[Si(CH_3)_3]_2]_2$	1130
$[SeN[Si(CH_3)_3]_2]_2$	1029
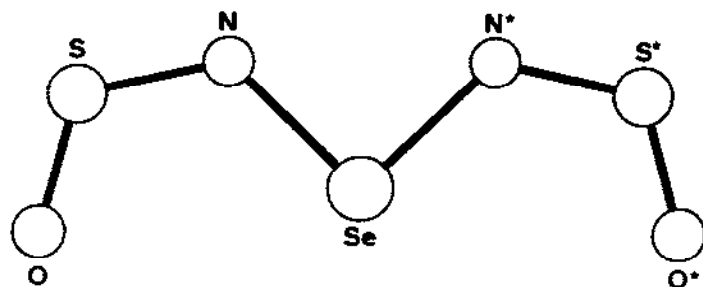
Fig. 38. Structure of Se(NSO)₂; m.p. 122°C.

$$CF_3SeNH_2 + 4\,SO_2 \xrightarrow[\text{sieve } A_4]{\text{molecular}} CF_3SeNSO \tag{63}$$

All of them are moisture-sensitive, and $C_6H_2(CF_3)_3SeNSO$ decomposes in moist air with SO_2 elimination according to eqn. (64).

$$2\,C_6H_2(CF_3)_3SeNSO \xrightarrow[-SO_2]{} [C_6H_2(CF_3)_3SeN]_2S \tag{64}$$
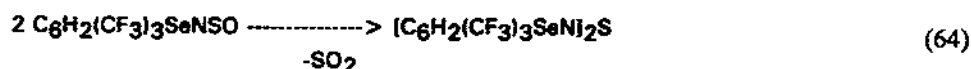
This compound is also obtained from the reaction of $[Me_3SiN]_2S$ with 2 equiv. of $C_6H_2(CF_3)_3SeCl$ [119] (Table 12). Apart from the SeNSO derivatives, only two Se^{II}-azides are described in the literature [120] (eqn. (65)).

$$RSeCl + (CH_3)_3SiN_3 \xrightarrow{\hspace{2cm}} RSeN_3 + (CH_3)_3SiCl \tag{65}$$
$$(R = C_6H_5, 2,4,6\text{-}(CH_3)_3C_6H_2^-)$$
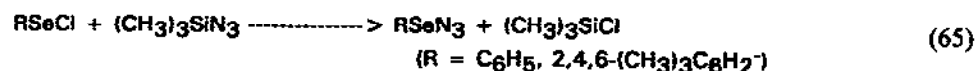
Whereas $C_6H_5SeN_3$ is unstable and decomposes with formation of $[C_6H_5Se]_2$ and N_2, the more hindered mesityleneselenyl azide is stable for a few hours at room temperature. The metathesis of tris(trimethylsilyl)amine with 3 equiv. of benzeneselenyl chloride provides

Fig. 39. Structure of $C_6H_4(CF_3)_3SeNSO$, m.p. 103°C.

TABLE 12

^{77}Se NMR shifts of SeNSO containing compounds

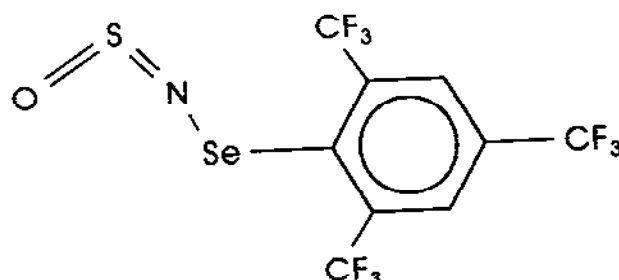| Compound	δ
Se(NSO)$_2$	1390 [143]
CF$_3$SeNSO	1091
C$_6$H$_2$(CF$_3$)$_3$SeNSO	929

the stable (C$_6$H$_5$Se)$_3$N (eqn. (66), a low melting orange solid characterized by ^{77}Se NMR spectroscopy and elemental analysis [120].

$$3\ C_6H_5SeCl + (CH_3Si)_3N \relbar\joinrel\relbar\joinrel\joinrel\longrightarrow (C_6H_5Se)_3N + 3\ (CH_3)_3SiCl \tag{66}$$

(b) Se^{IV}–N compounds

These compounds are derivatives of seleninic acids. Pyrolysis of F$_3$CSeO$_2$NH$_4$ in the presence of NH$_3$ provides F$_3$CSe(O)NH$_2$ in quantitative yield, which was characterized by IR and NMR spectroscopy (^{1}H, ^{19}F). Reaction of F$_3$CSe(O)NH$_2$ with SOCl$_2$ gives the corresponding –SeNSO derivative [118] (eqn. (67)).

$$F_3CSe(O)NH_2 + SOCl_2 \relbar\joinrel\relbar\joinrel\longrightarrow F_3CSe(O)NSO + 2\ HCl \tag{67}$$

F$_3$CSe(O)NSO occurs as colourless needles melting at 39.5°C. Due to its volatility, a gas phase IR spectrum was obtained: 1223s, 1185vs, 1106vs, 1076w,sh, 948s, 736m cm^{-1} [118].

(c) Se^{VI}–N compounds

Only a few Se^{VI}–N compounds have been synthesized due to the fact that only fluorine and oxygen are able to stabilize Se^{VI} compounds. In 1958, the synthesis of the C$_5$H$_5$NSeO$_3$-adduct and NH$_4$SeO$_3$NH$_2$ (eqn. (68)) were performed and the compounds characterized by elemental analysis [121].

$$C_5H_5N + SeO_3 \relbar\joinrel\longrightarrow C_5H_5N \cdot SeO_3 \xrightarrow{\ +\ 2\ NH_3\ } C_5H_5N + NH_4SeO_3NH_2 \tag{68}$$
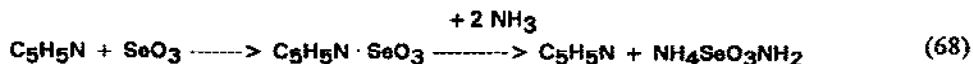
In contrast to F$_5$TeNH$_2$ (see Section B(ii)(d)), a good starting material for preparation of the corresponding F$_5$TeN derivatives, F$_5$SeNH$_2$ does not exist. F$_5$SeNCO is the only F$_5$SeN compound known, and is obtained by eqn. (69) [122,123].

$$Xe(OSeF_5)_2 + HCN \relbar\joinrel\relbar\joinrel\longrightarrow Xe + HOSeF_5 + F_5SeNCO \tag{69}$$

Pure F$_5$SeNCO is very explosive. Its characterization was done by mass spectrometry, ^{19}F NMR spectroscopy and elemental analysis. In 1990, the reaction of the silver salt of tri-

fluoromethylselenonic acid with C_2H_5I followed by $(CH_3)_2NH$ yielded the acid amide) which is stable only in solution (eqns. (70) and (71)). Characterization was carried out by NMR spectroscopy (^{19}F, ^{13}C, ^{77}Se). $C_6F_5Se(O)_2N(CH_3)_2$ was prepared in a similar manner [124].

$$RSeO_3Ag + C_2H_5I \text{--------} > RSeO_3C_2H_5 + AgI \qquad R = CF_3; C_6F_5 \tag{70}$$

$$RSeO_3C_2H_5 + (CH_3)_2NH \text{--------} > RSe(O)_2N(CH_3)_2 + C_2H_5OH \tag{71}$$
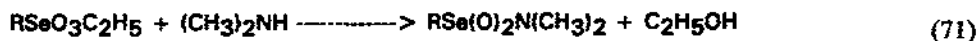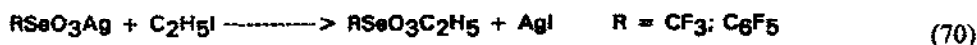
(iii) Acyclic compounds containing Se=N double bonds

In the past two decades, many examples of acyclic compounds containing discrete nitrogen–selenium double bonds have been prepared. The first of these was reported in 1967 and involved the preparation of ((arylsulfonyl)imino)selenyl dichlorides by eqn. (72) [125].

$$RSO_2NCl_2 + Se \text{--------} > RSO_2N=SeCl_2 \tag{72}$$

In 1973, a number of derivatives of N-substituted dichloroseleniumimides $R_2N=SeCl_2$ were obtained by reaction of N,N-dichloroamines and N,N-dichloroamides with elemental selenium or selenium tetrachloride. Characterization was carried out by infrared spectroscopy as well as elemental analysis [$R = (CH_3)_3C$, $(CH_3)_2(CN)C$, $(CH_3)(C_2H_5)(CN)C$, $(CH_2)_4C(CN)$, $(CH_2)_5C(CN)$, $C_2H_5OC(O)$, $(C_2H_5O)_2P(O)$, $C_6H_5SO_2$, p-$CH_3C_6H_4SO_2$, p-$ClC_6H_4SO_2$, p-$NO_2C_6H_4SO_2$] [126]. In the same year, the corresponding disubstituted selenium diimides were prepared. Reaction of SeF_4 with disilylated amides (eqn. (73) provides the following diimides ($R = C_6H_5SO_2$, C_6H_5CO, CH_3CO) [127].

$$SeF_4 + 2 RN[Si(CH_3)_3] \xrightarrow{\text{--------}} RN=Se=NR \tag{73}$$
$$-4 (CH_3)_3SiF$$
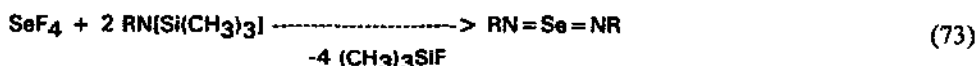
Further derivatives were reported in 1976, by reactions of $SeCl_4$ with 2 equiv. of tert-butylamine and p-toluenesulfonamide (eqn. (74) (R = ^tBu, Ts) [128].

$$SeCl_4 + 2 R\text{-}NH_2 \xrightarrow[\text{-4 HCl}]{CH_2Cl_2; Et_3N} R\text{-}N=Se=N\text{-}R \tag{74}$$
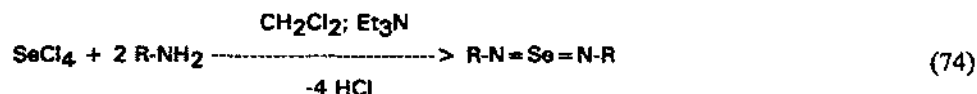
The synthesis of unsymmetric N,N'-disubstituted selenium diimides was mentioned for the first time in 1978. They were obtained by the reaction of N,N-bis(trimethylsilyl)amides with N-arylsulfonyldichloroselenimides (eqn. (75)) [129].

$$RN[Si(CH_3)_3] + ArSO_2N=SeCl_2 \xrightarrow[\text{-(CH_3)_3SiCl}]{\text{--------}} RN=Se=NSO_2Ar \tag{75}$$
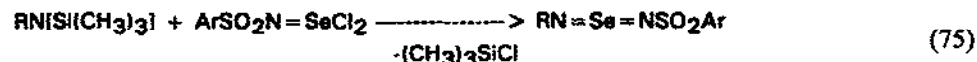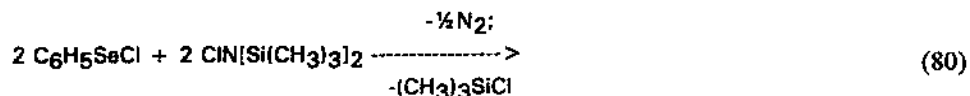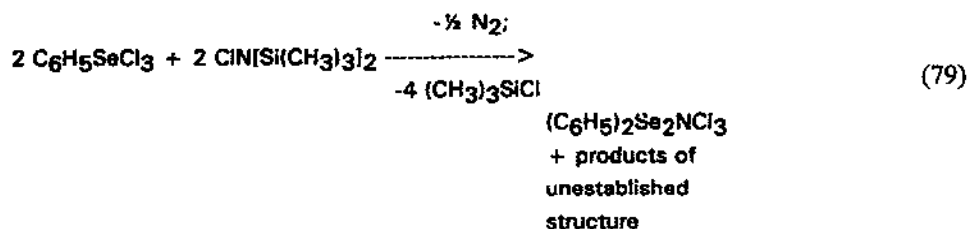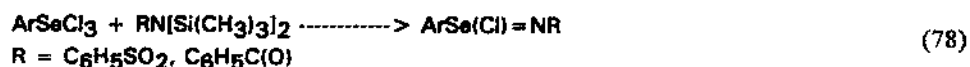
These compounds were characterized by elemental analysis and IR spectroscopy. Vibrations assigned to $\nu(\text{Se}=\text{N})$ are found in the range of 880–865 cm^{-1} [129]. Iminoselenium dichlorides, $R_2N=\text{SeCl}_2$, containing perfluorinated aryl-substitutes were synthesized for the first time in 1980 according to eqn. (76) (X = C(O), SO$_2$) [130].

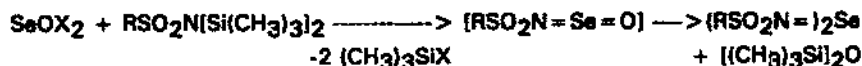$$\text{Se} + C_6F_5\text{XNCl}_2 \text{--------}> C_6F_5\text{XN} = \text{SeCl}_2 \qquad X = \text{CO, SO}_2 \tag{76}$$

Apart from the hitherto described Se=N containing compounds, the latter were characterized by ^{19}F NMR spectroscopy [130]. In 1982, the chemical behaviour of selenium diimides became the subject of intensive investigation. Reactions of $(C_6H_5SO_2N=)_2\text{Se}$ with aldehydes, dimethylsulfoxide, diphenylselenone, diphenylseleniumoxide, and triphenylphosphinoxide resulted in the oxygen atom being substituted by a phenylsulfonylimino group [131] (eqn. (77)).

$$½ (C_6H_5SO_2N=)_2\text{Se} + R=O \text{----------------}> \underset{-½\text{SeO}_2}{R=\text{NSO}_2C_6H_5} \tag{77}$$
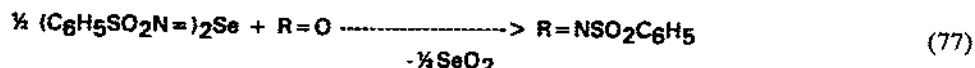
N-Aryldichloroselenoareneseleninimidoyl chlorides are obtained by the reaction of equimolar amounts of arylselenium chloride, arylselenium trichloride, and N-chlorohexamethylsilazane or by reaction of arylselenium trichlorides with N-chlorohexamethyldisilazane or hexamethyldisilazane (eqns. (78)–(80)) [132].

$$\text{ArSeCl}_3 + \text{RN[Si(CH}_3)_3]_2 \text{-----------}> \text{ArSe(Cl)} = \text{NR} \atop R = C_6H_5SO_2, C_6H_5C(O) \tag{78}$$

$$2 C_6H_5\text{SeCl}_3 + 2 \text{ClN[Si(CH}_3)_3]_2 \underset{-4 (\text{CH}_3)_3\text{SiCl}}{\overset{-½ \text{N}_2;}{\text{---------------}}}> \tag{79}$$

$(C_6H_5)_2\text{Se}_2\text{NCl}_3$
+ products of
unestablished
structure

$$2 C_6H_5\text{SeCl} + 2 \text{ClN[Si(CH}_3)_3]_2 \underset{-(\text{CH}_3)_3\text{SiCl}}{\overset{-½\text{N}_2;}{\text{---------------}}}> \tag{80}$$

Stable compounds (Se$_2$NCl$_3$R with R = C$_{12}$H$_{12}$, C$_{13}$H$_{12}$, C$_{14}$H$_{14}$, C$_{12}$H$_9$Cl, C$_{12}$H$_8$Cl$_2$) were characterized by IR spectroscopy and elemental analysis [132]. Whereas N-sulfinylsulfonamides RSO$_2$N=S=O have been known for a comparatively long time [133], the selenium analogues of these compounds RSO$_2$N=Se=O were unknown. The reaction of selenyl fluoride with N,N-bis(trimethylsilyl)sulfonamides yielded (RSO$_2$N=)$_2$Se according to eqn. (81).

$$SeOX_2 + RSO_2N[Si(CH_3)_3]_2 \xrightarrow[-2\ (CH_3)_3SiX]{} [RSO_2N=Se=O] \longrightarrow (RSO_2N=)_2Se + [(CH_3)_3Si]_2O$$

$$R = CH_3, C_6H_5 \qquad X = F, Cl \tag{81}$$
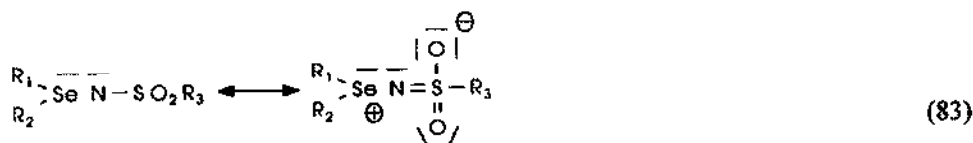
But the postulated intermediate $[RSO_2N=Se=O]$ could not be isolated. Difluoroselenium imides were obtained by the reaction of selenium tetrafluoride with disilylated amides in a 1:1 molar ratio (eqn. (82)) [134].

$$SeF_4 + C_6H_5SO_2N[Si(CH_3)_3]_2 \xrightarrow[-2\ (CH_3)_3SiF]{} C_6H_5SO_2N=SeF_2 \tag{82}$$
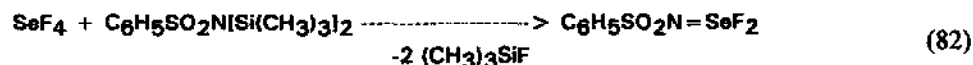
The first stable $R-N=Se=O$ species was prepared by reaction of $SeOCl_2$ with $^tBuNH_2$ in Et_2O at $-10°C$. $^tBu-N=Se=O$ is a brown moisture-sensitive oil, which was characterized by IR and NMR spectroscopy (^1H, ^{13}C) and mass spectrometry ($M = {}^tBu-N=Se=O \cdot H_2O$) [73]. At the same time, the hitherto poorly characterized $(^tBuN)_2Se$ was prepared and characterized by IR, NMR (^1H, ^{13}C) spectroscopy and mass spectrometry. Consistent with its sulfur analogue, $S(N^tBu)_2$ [135,136], $Se(N^tBu)_2$ at $-30°C$ displays Z/E-isomerism.

The preparation of two other unstable selenodiimines were reported in 1986. Reaction of $[(CH_3)_3Si]_2NSeCF_3$ with SeX_4 or SeO_2X_2 ($X = F$, Cl) probably provides $CF_3SeN=Se=NSeCF_3$, which immediately decomposes to $[CF_3Se]_2$, Se_8 and N_2. The bis-silylated selenodiimine, accessible by reaction of $LiN[Si(CH_3)_3]_2$ with $SeOCl_2$, reacts with 2 equiv. of $C_6H_5SO_2Cl$ to the well known $(C_6H_5SO_2N=)_2Se$ [137]. By means of model substances, such as $(C_6H_5)_2Se=NSO_2C_6H_4X$ ($X = H$, Cl, NO_2), $XC_6H_4(Cl)$ $Se=NSO_2Ph$ ($X = H$, Br, NO_2) or $Cl_2Se=NSO_2C_6H_4X$ ($X = CH_3$, H, Cl), an assignment of the bands for the stretching vibrations of the Se–N bonds and N–S^{VI} bonds was made on the basis of the shifts of the bands in the IR spectra of N-sulfonylchalcogenimides with ^{15}N-isotope substitution and previously obtained data from X-ray crystallographic analysis of these compounds. It was shown that N-sulfonylchalcogenimides have a bipolar structure (eqn. (83))[138].

$$\begin{array}{c} R_1 \\ R_2 \end{array}\!\!>\!Se-N-SO_2R_3 \quad\longleftrightarrow\quad \begin{array}{c} R_1 \\ R_2 \end{array}\!\!>\!\overset{}{Se}\overset{\ominus}{-}N=\overset{\overset{\textstyle |\,\overset{\ominus}{O}\,|}{|}}{\underset{\underset{\textstyle \diagdown O \diagup}{\parallel}}{S}}-R_3 \tag{83}$$

In contrast to arylsulfonyl-, $RSO_2N=SeCl_2$ [125], or pentafluorosulfanyl-iminose-lenyl dichlorides [139], which decompose upon standing, the pentafluorotellurium compound, $F_5TeN=SeCl_2$ [140] (see Section B(ii)(d)), is stable. It is accessible by reaction 84.

$$TeF_5NH_2 + SeCl_4 \xrightarrow{} TeF_5N=SeCl_2 + 2\ HCl \tag{84}$$
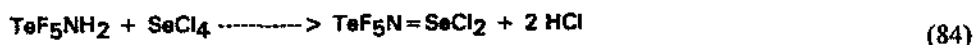
In order to prepare perfluoroalkyl analogues, one would envision either the free amines or the dichloroamines as precursors. Using dichloroamines possible HF-elimination to the corresponding nitriles could be circumvented. The reaction of BrCN with ClF gives an efficient method for producing CF_3NCl_2 which, as well as $C_2F_5NCl_2$) reacts readily with Se_2Cl_2 to give the corresponding $RN=SeCl_2$ [141] (eqn. (85)).

$$3\ RNCl_2\ +\ 2\ Se_2Cl_2\ \xrightarrow{\ \ \ \ \ CCl_3F\ \ \ \ \ }\ 3\ RN=SeCl_2\ +\ SeCl_4 \tag{85}$$

$CF_3N=SeCl_2$ and $C_2F_5N=SeCl_2$ were characterized by mass spectrometry and IR and NMR (^{19}F, ^{77}Se) spectroscopy. Both compounds decompose identically within 30 min at room temperature with elimination of $SeCl_4$ to give $RN=Se=NR$ and further Se as well as $RN=NR$, which is an overall decomposition to $RN=NR$ and Se_2Cl_2 [141].

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