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FLUOROCARBON-SELENIUM CHEMISTRY: ACCOMPLISHMENTS AND QUESTS

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SUMMARY

The binary selenium fluorides SeF_n (n = 2, 4, 6) and Se_2F_2 are considered along with corresponding perfluorohalogenoorganoselenium compounds with selenium in the oxydation states 1, 2, 4 and 6. For lower selenium fluorides, preparation and characterisation are emphasized. Recent results in the chemistry of $SeCF_2$, CF_3SeCl, $CF_3SeSeCF_3$, $CF_3Se(O)OM$ and CF_3Se^{VI}- compounds are presented. A comparison with the corresponding sulfur chemistry is also provided.

INTRODUCTION

It is rather surprising that the two elements S and Se, although neighbours in the 6th main group, have so differently attracted interest of preparative chemists. While the chemistry of sulfur is under investigation in laboratories all over the world, only a few research groups have shown interest in the covalent chemistry of selenium and its compounds. This discrepancy can be attributed to the high industrial and therefore public interest, to the higher natural abundance and a low price for sulfur, and to the fact that sulfur compounds are used industrially on a large scale in many fields.

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In addition, selenium compounds are normally extremely toxic and exhibit a penetrating odour. They are therefore not very attractive substances. Consequently, the broad knowledge in sulfur chemistry serves as the foundation for chemists who have research interests in selenium. It is the main task of this article to demonstrate how closely the chemistry of selenium parallels that of sulfur, especially in the field of perfluoroorgano compounds.

RESULTS AND DISCUSSION

Basic molecules in this area are the halides, among them the fluorides. In the last ten years very little preparative work has been carried out with selenium-chlorides, -bromides and-iodides and no binary Se-F compounds in lower oxidation states are known. A completely different situation exists for the sulfur fluorides in lower oxidation states. Since the full characterisation of SF_2 [1] and its dimer F_3SSF [2], which was isolated for the first time in a pure state in 1980, as well as the preparation of $F_3S{\cdot}SSF$ via $F_2S{=}S + SF_2$ by Willner [3], the investigation of the lower sulfur fluorides has come to a standstill. This leaves the question open to what is possible in the corresponding selenium chemistry.
The results achieved up to now in the chemistry of lower sulfur fluorides encouraged us to tackle the problem of preparation and characterisation of Se_xF_2. Attempts to fluorinate $SeCl_2$ or Se_2Cl_2 with AgF or highly dispersed KF led only to SeF_4. Another method used to synthesize lower Se-fluorides is the reaction of selenium vapour with F_2, highly diluted with Argon. When Se is reacted with F_2 under matrix conditions, a mixture of compounds is formed according to

$$Se_{vapour} + (F_2 + Ar) \xrightarrow{(1:200 \text{ to } 1:10^3)} Se_xF_2$$

After blanks proved that in the absence of F_2 or Se vapour no absorptions were present in the IR-matrix spectrum, a spectrum of the reaction products was taken. The upper spectrum in Fig. 1 shows very convincingly that new absorptions appear besides those known for the SeF_4-bands. In order to determine whether or not these new bands belonged to one or more Se-F compounds, reactions were repeated with variation of temperature and /or the F_2/Ar ratio. It was possible to show that varying these conditions results in a

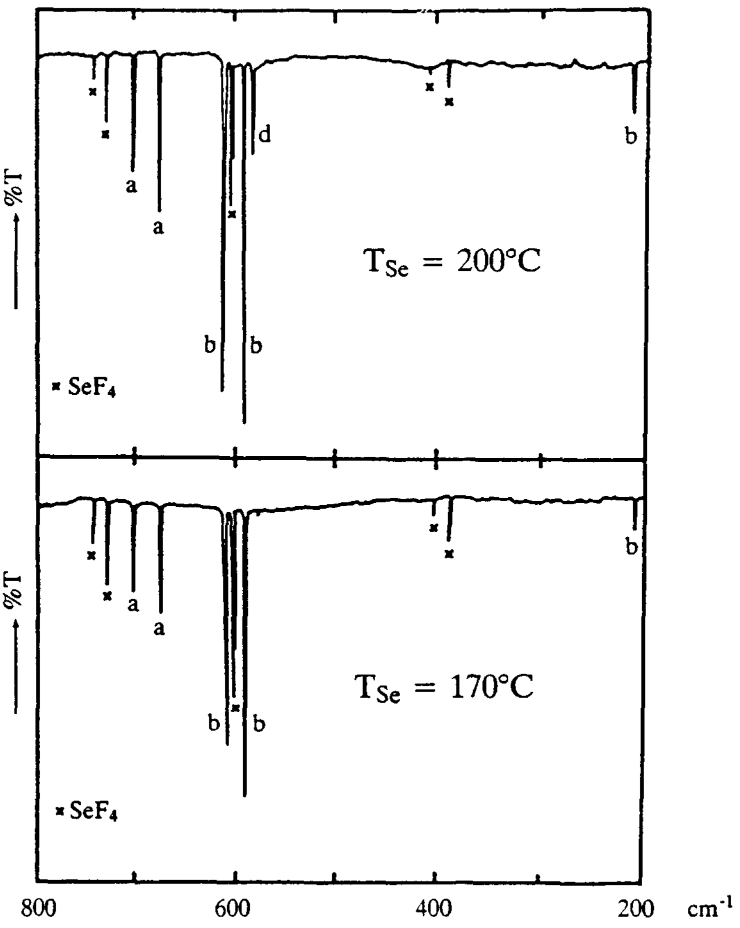
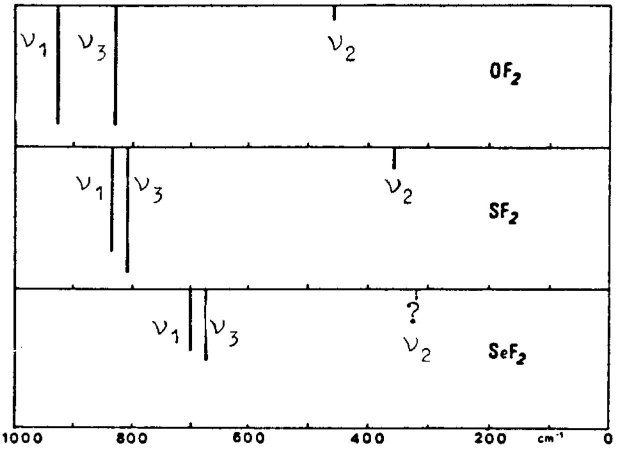


Fig. 1. IR matrix spectra of F_2 : Ar (1 : 500) + Se reaction pruducts at 200 and 170°C.

change of intensities of absorption bands. The lower spectrum of Fig. 1 represents such an experiment at 170°C. It illustrates how decreasing the temperature from 200 to 170°C at a constant Se/F_2/Ar ratio leads to decreased intensities of bands 'a' and 'b', with concomitant increase in the SeF_4 absorptions.

An experiment with an equilibrated 1 : 1 selenium isotopic mixture of highly enriched ^{76}Se and ^{82}Se at 200°C provided isotopic patterns for individual band envelopes shown in Fig. 2. The 'a' bands split into doublets and the b bands into triplets. This casts some light on the symmetry and the number of bonded Se-atoms in the molecules obtained.

Band group a appears in the equatorial Se-F stretching vibration region of SeF_4 and consists of two bands. One can assign these two bands to Se-F stretching vibrations. On the other hand, selenium isotopic substitution results in two doublets, thus proving the presence of only one Se atom in the molecule. Consequently, the only structure possible for the latter is SeF_2 with C_{2v} symmetry. Additional, evidence for the proposed structure can be derived from the measured positions and relative intensities of the bands in the series OF_2, SF_2, SeF_2 shown below.



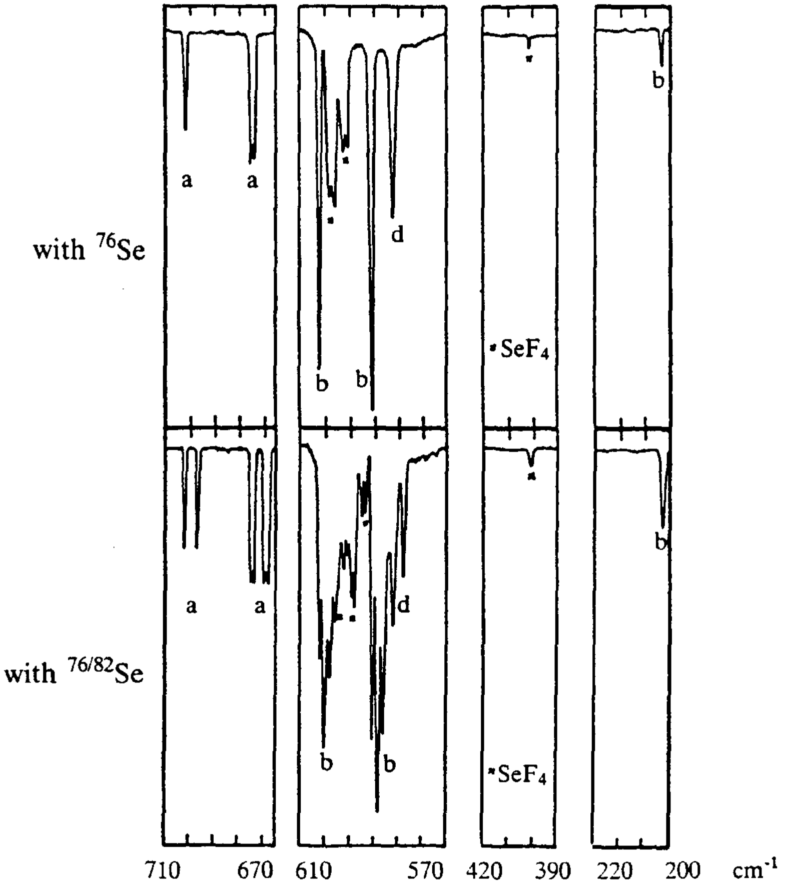
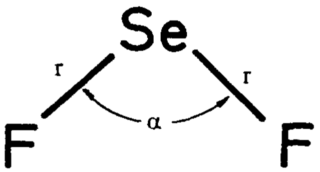


Fig. 2. IR matrix spectra of F$_2$: Ar (1 : 500) + ^{76}Se and $^{76/82}$Se reaction products at 200°X.

By analogy with SF$_2$, $\nu_1 > \nu_2$ is assigned. The bond angle calculated including ν_3 and the selenium isotopic shift is α = 94.0 ± 0°. With an assignment $\nu_2 > \nu_1$, the calculated bond angle α = 85.7 ± 1° is not realistic. The deformation mode ν_3 which was too weak to be observed, was estimated to 320 cm^{-1}. Molecular data gained from the vibrational frequences are as follows:



$r = 1.69$ Å*

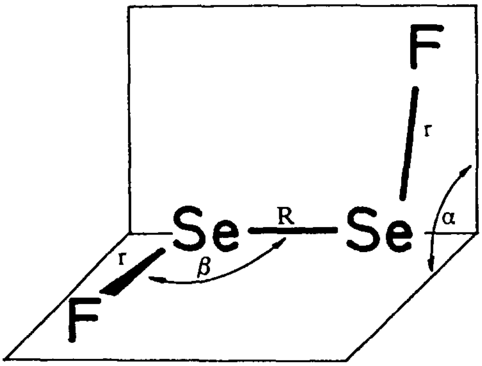
$\alpha = 94°$

	[cm^{-1}]	Assignment	
ν_1	702.0/697.2	ν_s	$^{76/82}$Se
ν_2	320*	δ	
ν_3	675.0/669.8	ν_{as}	$^{76/82}$Se

* estimated; $f_r = 4.29$; $F_{rr} = 0.24$ mdyn/Å

Analysis of the band group b in Fig. 2 helped to elucidate the structure of the species b. From the number of IR active stretching vibrations one can assume the existence of two Se-F bonds that cannot be trans to each other. The selenium isotopic substitution led to beautifully resolved triplets for these vibrations. This is only possible under the condition that the molecule contains two equivalent selenium atoms. Thus, it is most likely that we are dealing here with a chain molecule of FSeSeF structure having C_{2v} or C_2 symmetry. Three fundamentals measured out of six possible were, by analogy with FSSF [4], assigned to ν_1, ν_5, ν_6. The bands ν_1 and ν_5 are placed in the stretching vibration range of axial X-F (X = S, Se) bands of XF_4. The intensity ratios $\nu_1 : \nu_5 : \nu_6$ for FSSF and FSeSeF are similar to each other. The last remark gives support to C_2 symmetry for the molecule, yet C_{2v} symmetry cannot be excluded at this stage.

Estimated molecular parameters of FSeSeF and calculated force constants are given:



estimated structure:
R = 2.25 Å
r = 1.77 Å
ß = 100°
α = 90°

calculated force constants: f_r = 3.25, f_{rr} = 0.13 mdyn/Å

On the basis of the molecular parameters, and on both measured and estimated frequences, normal coordinate analysis was performed. Both calculated and observed frequences are in good agreement thus making the adopted model very probable. UV-photolysis of the mixture of binary selenium fluorides frozen in a Noble gas matrix leads to a decrease in the intensity of vibrations assigned to FSeSeF. At the same time a new group of bands 'c' appears, reaching a maximum after several minutes, as shown in Fig. 3. The four additional absorptions measured are assigned to $Se=SeF_2$ by analogy with the UV photolysis of FSSF that results also in the structural isomer $S=SF_2$ [4]. Moreover, the $^{76/82}Se$ isotopic pattern of individual bands fits well with the calculated model. The two ν(Se-F) vibrations are split into two doublets and a triplet occuring in the ν(Se=Se) region. The fourth band shows no splitting, due to a small isotopic effect.

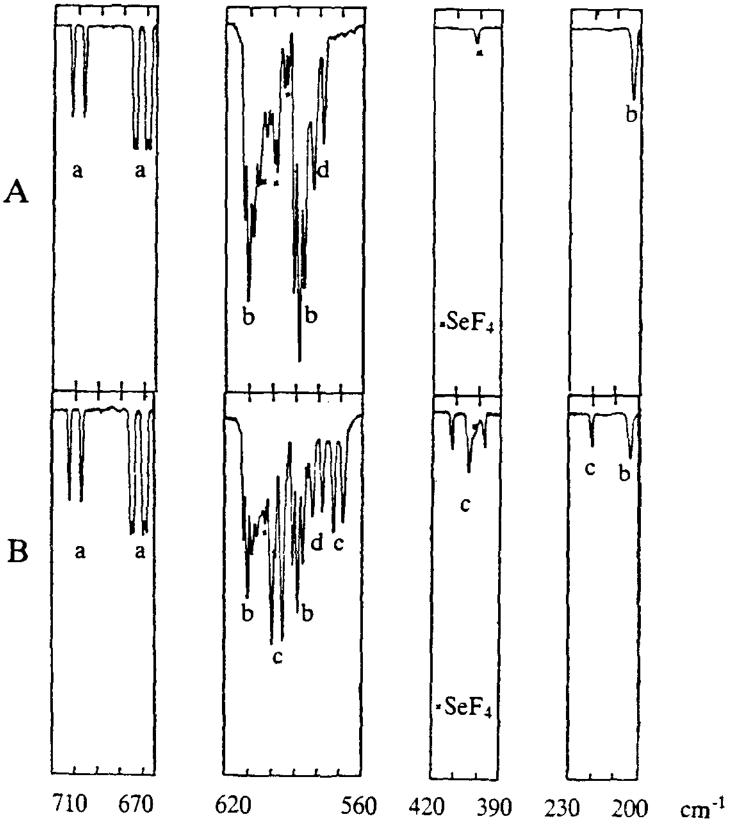
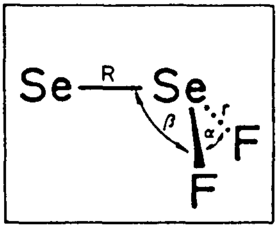


Fig. 3. A: IR-Matrix spectrum of F_2 and $^{76/82}$Se at 200°C.

B: Spectrum A after 5 minutes UV-photolysis.

Estimated molecular parameters of Se=SeF_2 and calculated force constants are presented below.



estimated structure

R = 2.15 Å   r = 1.77 Å

α = 90°   β = 100°

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calculated force constants

f_R = 3.67 f_r = 3.07 f_{rr} = 0.14 mdyn/Å

Normal coordinate analysis was tackled by the classical Wilson F-G-matrix method and provided a good fit with the experimental frequences [5].

In contrast to the lower sulfur fluorides, nothing is known about the chemical and physical properties of lower selenium fluorides up to now. Substitution of F with CF_3 leads to CF_3SeF, an unknown molecule. The only evidence available so far for the existence of CF_3SeF is the reactions shown below.

CF_3SeCl + AgF →

<CF_3SeF> → $CF_3SeSeCF_3$ + CF_3SeF_3 (CF_3SeO_2H)

$CF_3SeN(CH_3)_2$ + 2 HF →

CF_3SeF could not be detected in any of these reactions. It seems to behave similarly to CF_3SF [6], especially in the presence of catalytic amounts of HF, disproportionating into $CF_3SeSeCF_3$ and CF_3SeF_3. By reaction with traces of H_2O, CF_3SeO_2H is also formed. Nothing is known about intermediates in this disproportionation [7].

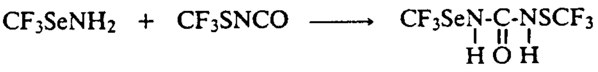
Well known and rather common are the molecules CF_3SeCl and CF_3SeBr. They are widely used to synthesize CF_3Se compounds, especially CF_3Se derivatives of N, P and As. While the reaction of CF_3SeX (X = Cl, Br) with NH_3 depending on conditions leads to $(CF_3Se)_nNH_{3-n}$, the corresponding $(CF_3Se)_3M$ are made from MBr_3 and $Hg(SeCF_3)_2$ with M = P and As.

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

n	T [°C]	t [h]	$CF_3SeBr:NH_3$	yields [%]
3	-10	2-3	3:4	30
2	-20	6	2:3	61
1	- 0	1	1:3	22.5

$$2\,(CF_3Se)_3N \xrightarrow{CF_3SeX} 3\,CF_3SeSeCF_3 + N_2$$

The above scheme provides reaction conditions and yields for the preparation of $(CF_3Se)_nNH_{3-n}$. Using excess CF_3SeBr for the preparation of $(CF_3Se)_3N$ does not lead to a higher yield but on the contrary to lower yields because side reactions are obtained. It was possible to show that $(CF_3Se)_3N$ in the presence of CF_3SeBr decomposes to $CF_3SeSeCF_3$ and N_2. Typical reactions of the amines are presented below.



$$CF_3SeNH_2 + CF_3SNCO \longrightarrow CF_3Se\underset{\underset{H}{|}}{N}\text{-}\underset{\underset{O}{\|}}{C}\text{-}\underset{\underset{H}{|}}{N}SCF_3$$

$$(CF_3Se)_3N + (C_6H_5)_3P \longrightarrow CF_3SeN{=}P(C_6H_5)_3 + CF_3SeSeCF_3$$

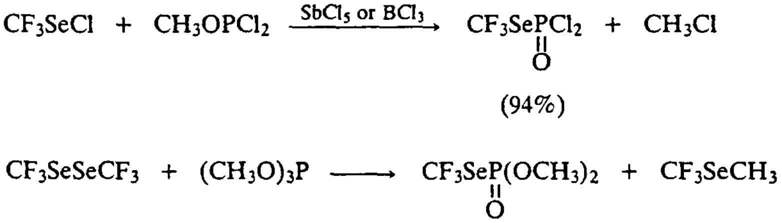
$$MBr_3 + Hg(SeCF_3)_2 \longrightarrow (CF_3Se)_3M + CF_3SeHgBr$$
M = P, 79%; M = As, 65.7%

$$P_2I_4 + Hg(SeCF_3)_2 \longrightarrow (CF_3Se)_2P\text{-}P(SeCF_3)_2 + (CF_3Se)_3P$$

The amine forms with CF_3SNCO the corresponding urea derivative and, with triphenylphosphane, $(CF_3Se)_3N$ gives $CF_3SeN{=}P(Ph)_3$ and $CF_3SeSeCF_3$. This behaviour is completely matched by $(CF_3S)_nNH_{3-n}$. In order to obtain $(CF_3Se)_3M$ (M = P, As), an excess of $Hg(SeCF_3)_2$ is reacted with MX_3 in CS_2 at 20°C. Partial substituted products such as $(CF_3Se)_2PBr$ or $(CF_3Se)_2AsCl$ are detected by ^{19}F-NMR-spectroscopy when PBr_3 or $AsCl_3$ are reacted with $Hg(SeCF_3)_2$ in molar ratios of 2 : 3 or 1 : 5 respectively.

Analogously, P_2I_4 reacts with $Hg(SeCF_3)_2$ in CS_2 to yield a mixture of $(CF_3Se)_2P{-}P(SeCF_3)_2$ and $(CF_3Se)_3P$. The thermally unstable diphosphane can be purified by fractional condensation to a 90 to 95 % purity [8].

In agreement with CF_3SCl and CF_3SSCF_3, the corresponding selenium compounds react with CH_3OPCl_2 [9] and $(CH_3O)_3P$ [10] in an Arbuzov type of reaction to form the corresponding phosphoric esters as shown below.



$$CF_3SeCl + CH_3OPCl_2 \xrightarrow{SbCl_5\text{ or }BCl_3} CF_3Se\underset{\underset{O}{\|}}{P}Cl_2 + CH_3Cl$$

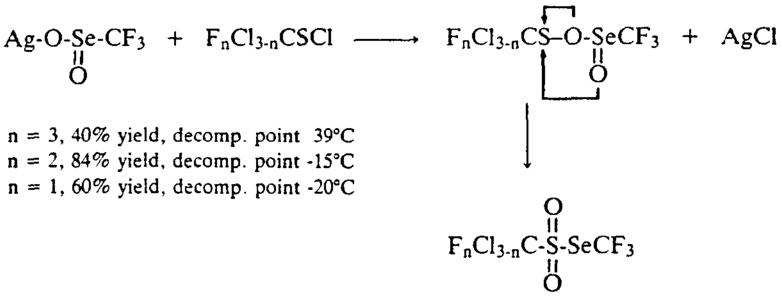
(94%)

$$CF_3SeSeCF_3 + (CH_3O)_3P \longrightarrow CF_3Se\underset{\underset{O}{\|}}{P}(OCH_3)_2 + CF_3SeCH_3$$

Good yields of $CF_3SeP(O)Cl_2$ [9] are only obtained at -10 to +5°C in the presence of stoichiometric amounts of $SbCl_5$ or BCl_3. In these Arbuzov reactions the CF_3Se group behaves like chlorine.

Contrary to CF_3S chemistry, no compounds of the formula CF_3SeSeX (X = F, Cl) are known so far.

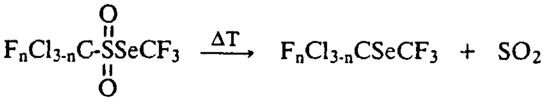
An interesting new type of reaction is found in CF_3Se^{IV}-chemistry since it was possible to show that $AgOSe(O)CF_3$ reacts with $F_nCl_{3-n}CSCl$ at temperatures between -80 and 0°C according to



n = 3, 40% yield, decomp. point 39°C
n = 2, 84% yield, decomp. point -15°C
n = 1, 60% yield, decomp. point -20°C

The corresponding mixed anhydrides F_nCl_{3-n} $CSOSe(O)CF_3$, unstable intermediates, rearrange in an intramolecular redox reaction to $F_nCl_{3-n}CS(O_2)SeCF_3$.

Thermal decomposition of the sulfones leads to selenides and provides an elegant synthetic route for the preparation of $CF_3SeCF_nCl_{3-n}$.



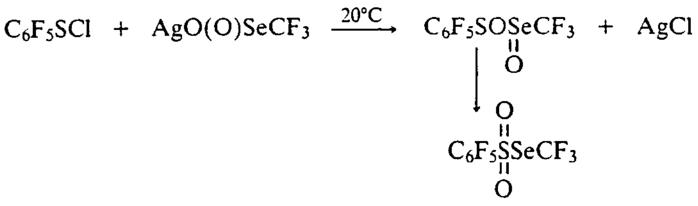
$$F_nCl_{3-n}C\text{-}S(O_2)SeCF_3 \xrightarrow{\Delta T} F_nCl_{3-n}CSeCF_3 + SO_2$$

For n = 3, ΔT = 160°C (20 h) in C_6F_6, 100% yield
n = 2, ΔT = 20°C in $CFCl_3$, 54% yield
n = 1, ΔT = 20°C in $CFCl_3$, 45% yield.

$$F_nCl_{3-n}CSO_2Cl + AgSeCF_3 \longrightarrow \text{no reaction.}$$

The possibility that the silver salt oxidizes primarily $F_nCl_{3-n}CSCl$ to $F_nCl_{3-n}SO_2Cl$ which reacts with the formed $AgSeCF_3$ to the final products was excluded by blanks.

A completely different behaviour is observed with C_6F_5SCl dissolved in CF_2ClCCl_2F in the reaction with $AgO(O)SeCF_3$. The products isolated here are the new $C_6F_5SO_2SC_6F_5$, $CF_3SeSeCF_3$ and $[F_3CSe(O)]_2O$ as shown below.



$$C_6F_5SCl + AgO(O)SeCF_3 \xrightarrow{20^{\circ}C} C_6F_5SO\underset{\underset{O}{\|}}{S}eCF_3 + AgCl$$

$$\downarrow$$

$$C_6F_5\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}SeCF_3$$

$$C_6F_5SO_2SeCF_3 + C_6F_5SCl \longrightarrow C_6F_5SO_2SC_6F_5 + CF_3SeCl$$

$$CF_3SeCl + AgO(O)SeCF_3 \longrightarrow CF_3SeSeCF_3 + [CF_3Se(O)]_2O + AgCl$$

In order to understand this reaction it is assumed that $C_6F_5SO(O)$-$SeCF_3$ which is first formed rearranged to $C_6F_5S(O_2)SeCF_3$ as expected. This reacts with excess of C_6F_5SCl to $C_6F_5SO_2SC_6F_5$ before SO_2 elimination takes place. In a blank reaction, it was shown that CF_3SeCl formed with $AgO(O)SeCF_3$ the anhydride and $CF_3SeSeCF_3$, in agreement with the observed products. This is a good method for preparation of $[CF_3Se(O)]_2O$ since only common reagents are used [7].

While CF_3SeCF_3 is oxidized by ClF to the known $(CF_3)_2SeF_2$ which on reaction with glass forms $(CF_3)_2SeO$, CF_3SeCF_2Cl and ClF react in a steel autoclave, then in glass to yield $CF_3Se(O)Cl$ and CF_3Cl as the final products. A general method to transform $(R_f)_2Se$ to $(R_f)_2SeO$ is found in oxidation of selenides to selenoxides by means of m-chloroperbenzoic acid as shown below.

$$CF_3SeCF_3 + 2\,ClF \xrightarrow[-Cl_2]{} CF_3SeF_2CF_3 \xrightarrow{SiO_2} (CF_3)_2SeO$$

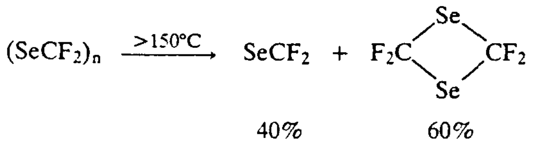
$$CF_3SeCF_2Cl + 2\,ClF \xrightarrow{SiO_2} CF_3Se(O)Cl + CF_3Cl$$

$$CF_3SeCF_nCl_{3-n} + 3\text{-}Cl\text{-}C_6H_4\text{-}C(O)OOH \longrightarrow CF_3Se(O)CF_nCl_{3-n}$$

$n = 3$. 98% yield; $n = 2$. 78% yield

In recent years new results in Se=C chemistry have been obtained. Since the first preparation of $SeCF_2$ by thermal decomposition of $B(SeCF_3)_3$ in the presence of KF [11], better methods have been published . In octamethylcyclotetrasiloxane, AlI_3 or better R_2AlI and $Hg(SeCF_3)_2$ react at 50 to 55°C to 70 % $SeCF_2$ [12]. It can also be made by thermal decomposition of $(CH_3)_3SnSeCF_3$ [13]. The first reaction in the scheme below provides $SeCF_2$ in 60 % yield but it is unstable above -80°C in the presence of BF_3 and polymerises. Separation by trap to trap distillation below -80°C is very tedious. So pyrolysis of the polymer is a more convenient method as the cyclic dimer is a solid and $SeCF_2$ can be removed without problems. The second method is very efficient and very easily carried out. Technically it can be compared with the preparation of CO_2 from a carbonate and an acid. This is also valid for the third reaction.

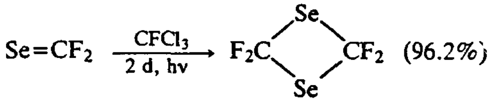
$$B(SeCF_3)_3 \xrightarrow{110°C/KF} \underset{60\%}{Se{=}CF_2} + BF_3$$

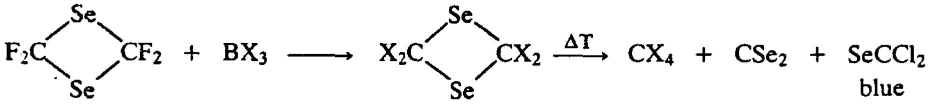


$$Hg(SeCF_3)_2 + AlI_3 \xrightarrow[{[(CH_3)_2Si\text{-}O\text{-}]_4}]{50\text{-}55°C/5\ Torr} SeCF_2\ (70\%)$$

$$(CH_3)_3SnSeCF_3 \longrightarrow \underset{100\%}{Se{=}CF_2} + (CH_3)_3SnF$$

Besides pyrolysis of the polymer $(SeCF_2)_n$, the dimer is also obtained in almost quantitative yield from the monomer dissolved in $CFCl_3$ during 2 days in sunlight [12]. Halogen exchange reactions with BX_3 lead to the formation of tetrahalogeno-1,3-diselaetanes with X = chlorine or bromine. They are stable substances at 25°C but decompose on heating to CX_4 and CSe_2 [11]. However, when the pyrolysis of $(Cl_2C\text{-}Se\text{-})_2$ is carried out in vacuo at 200°C, in addition to the known products, a blue substance condenses at -196°C. By means of mass-, low temperature UV-, IR matrix- and raman matrix spectra, this species was characterized as $SeCCl_2$. Above -130°C, it oligomerises to a colourless solid mixture [14].





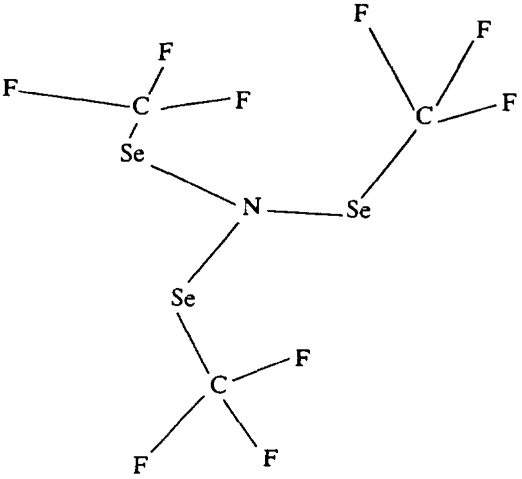
X = Cl, 96%; X = Br, ~95%.

Electron diffraction studies of $SeCF_2$ [14], $F_2CSe_2CF_2$ [15] and $(CF_3Se)_3N$ [16] provide structures and molecular parameters. The structures obtained are in good agreement with the vibrational spectra of the molecule. Figures 4 and 5 show geometry, bond distances and angles.

d(C=Se) = 1.743 (3) Å
d(C-F) = 1.314 (2) Å
∢(F-C-F) = 107.5° (0.4)
∢(Se-C-F) = 126.3° (0.2)

d(C-F) = 1.353 (3) Å
d(C-Se) = 1.968 (4) Å
d(Se...Se) = 2.98 (3) Å
∢(Se-C-Se) = 98.5° (4)
∢(F-C-F) = 106.3° (8)
∢(Se-C-F) = 126.3° (0.2)

Fig. 4. Structures and molecular parameters of $SeCF_2$ and its cyclic dimer.



d(C-F) = 133,6 pm
d(N-Se) = 183,9 pm
d(Se-C) = 187,1 pm
∢(Se-N-Se) = 119,2°
∢(F-C-F) = 108,2°
∢(N-Se-C) = 104,3°

$\tau_1 = 13 \pm 2°$
$\tau_2 = \tau_3 = 170 \pm 2°$

Fig. 5. Structures and molecular parameters of $(CF_3Se)_3N$.

Chemical properties of selenocarbonyldifluoride are comparable with those of SCF_2. It adds halogens to form α-halogenoselenylhalides with X = Cl, Br. Chlorination, even at -80°C, provides $SeCl_4$ and $F_2ClCSeCF_2Cl$ as by-products [11]. A tentative mechanism for their formation is oxidation of some $F_2ClCSeCl$ to $F_2ClCSeCl_3$ which forms with excess $F_2ClCSeCl$ the isolated by-products.

$$F_2C{=}Se + X_2 \longrightarrow F_2XCSeX \ (X = Cl, Br)$$

$$F_2ClCSeCl + Cl_2 \longrightarrow F_2ClCSeCl_3$$

$$F_2ClCSeCl_3 + F_2ClCSeCl \longrightarrow F_2ClCSeCF_2Cl + SeCl_4$$

It reacts with metal fluorides to give $MSeCF_3$. The Cs- and Tl-salts are unstable and are characterized by the reaction with $(C_6H_5)_2PI$ at -40°C providing $CF_3SeP(C_6H_5)_2$. The silver salt can also be made from $B(SeCF_3)_3$ and AgF at 150°C.

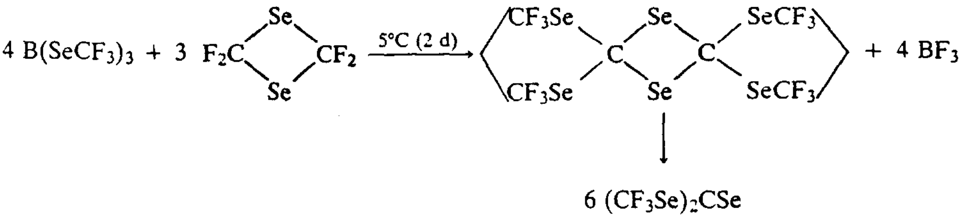
$$MF + Se{=}CF_2 \longrightarrow MSeCF_3 \quad M = Cs, Tl, (CH_3)_4N, Ag$$

$$\underset{M' = Cs,\ Tl}{M'SeCF_3} + (C_6H_5)_2PI \longrightarrow (C_6H_5)_2PSeCF_3 + M'I$$

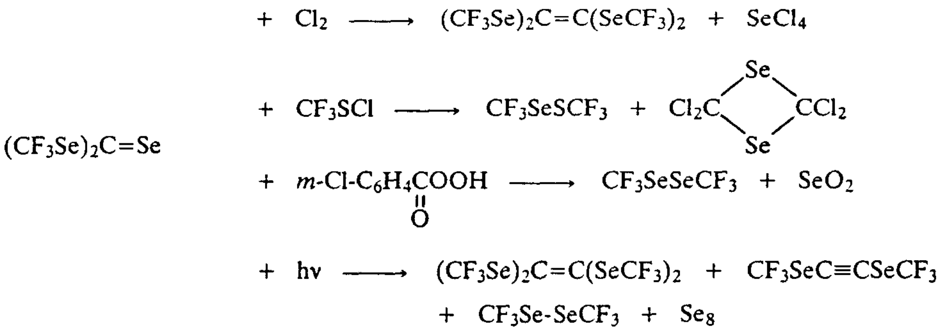
$$B(SeCF_3)_3 + 3\ AgF \xrightarrow{150°C} 3\ AgSeCF_3$$

The linear dimerisation and trimerisation of $SeCF_2$ is more complicated than that of SCF_2 and takes place in a different way.

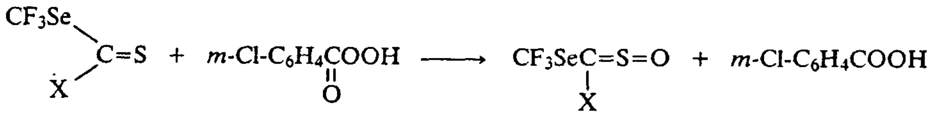
The reaction between tetrafluoro-1,3-diselaetan and $B(SeCF_3)_3$ leads to $(CF_3Se)_2C{=}Se$ probably via substitution of the 4 F atoms by CF_3Se-groups forming the tetrasubstituted four membered ring, which is unstable and decomposes to $(CF_3Se)_2C{=}Se$ according to



The synthesis of the linear dimer $CF_3SeC(=Se)F$ has not been achieved so far. The deep red coloured liquid (m.p. -7°C) $(CF_3Se)_2C=Se$ behaves chemically completely differently to its sulfur analogue as shown by the equations below.



Oxidation of CF_3Se substituted thiocarbonyls with meta-chloroperbenzoic acid provides the corresponding $>C=SO$ derivatives [17] according to



X = Cl, Br, SCF_3, $SeCF_3$

Another element with which Se is able to establish double bonds is nitrogen. Compounds of the type $F_5TeN=SeCl_2$ have been published by Seppelt and coworkers [18] and those of type $RN=SeX_2$ or $RN=Se=NR$ have been prepared by Derkach <u>et al.</u> [19]. In sulfur chemistry, $R_3SiN=S=NSiR_3$ is a commonly used starting material in preparative work. The corresponding Se-compound was synthesized from $(R_3Si)_2NLi$ and $SeOCl_2$ at -78°C in pentane, according to

$$2\,[(CH_3)_3Si]_2NLi + Se(O)Cl_2 \xrightarrow[\text{pentane}]{-78^\circ C} (CH_3)_3SiN{=}Se{=}NSi(CH_3)_3 + (CH_3)_3SiOSi(CH_3)_3 + 2\,LiCl$$

$$\begin{array}{lll} & \xrightarrow{-50^\circ C} & (CH_3)_3SiSi(CH_3)_3 + N_2 + Se_8 \\ (CH_3)_3Si{-}N{=}Se{=}N{-}Si(CH_3)_3 & & \\ & \xrightarrow{C_6H_5SO_2Cl} & C_6H_5SO_2N{=}Se{=}NSO_2C_6H_5 + 2\,(CH_3)_3SiCl \end{array}$$

$$2\,F_3CXN[Si(CH_3)_3]_2 + SeOCl_2 \longrightarrow F_3CXN{=}Se{=}NXCF_3 + 2\,(CH_3)_3SiCl + (CH_3)_3SiOSi(CH_3)_3$$

$X =$ C(O), SO_2

The existence of the unstable substance, which decomposes at -50°C, was proved by reaction with $C_6H_5SO_2Cl$ giving the stable known $C_6H_5SO_2N{=}Se{=}NSO_2C_6H_5$ [19]. Attempts to replace the R_3Si-groups by e.g. CF_3S failed and only decomposition products were observed even at low temperatures. Perfluorinated derivatives with the N=Se=N group are obtained from $CF_3XN(SiR_3)_2$ (X = CO, SO_2) and $SeOCl_2$. The two new seleno-(IV)-diimides are resonance stabilised and fully characterized [17].

A so far almost unwritten chapter in selenium chemistry concerns perfluoroorgano-selenium-(VI)-compounds. The only substances published so far are $C_2F_5SeF_4Cl$ and traces of $C_2F_5SeF_5$ prepared by Lau and Passmore [20]. Our main interest was concerned with the preparation of CF_3SeO_3H since CF_3SO_3H is already an important industrial chemical. Earlier attempts by Dale, Emelèus and Haszeldine [21] to prepare CF_3SeO_3H by oxidizing CF_3SeO_2H with 100 % H_2O_2 or conc. HNO_3 failed as demonstrated below.

$$C_2F_5SeF_3 + ClF \xrightarrow{-78^\circ C} C_2F_5SeF_4Cl$$

$$C_2F_5SeF_3 \cdot CsF + ClF \xrightarrow{-78^\circ C} C_2F_5SeF_5 \text{ (traces)}$$

$$CF_3SeO_2H + H_2O_2 \text{ (100\%) or } HNO_3 \text{ (conc.)} \longrightarrow \text{no } CF_3SeO_3H$$

Among the many oxidizing agents used by Haas and Weiler for the synthesis of CF_3SeO_3H, four are given together with observed reaction products below.

$$\begin{tikzcd} & CO_2 + H_2SeO_4 \\ CF_3SeO_2H \arrow[ur, "H_2O_2\ 30\%", "\text{reflux}"'] \arrow[r, "HClO_3\ 40\%"] \arrow[dr, "HOF"] & CO_2 + H_2SeO_4 \\ & CF_4 + H_2SeO_4 \end{tikzcd}$$

electrolysis:

$$CF_3SeO_2^- \xrightarrow[160^\circ C]{-e^-} [CF_3SeO_2\cdot] \longrightarrow 1/2\ C_2F_6 + SeO_2$$

They are: refluxing CF_3SeO_2H with 30 % H_2O_2, reacting it with 40 % $HClO_3$, HOF and anodic oxidation of $CF_3SeO_2^-$. In all cases, a rupture of the C-Se bond is observed giving H_2SeO_4 and CO_2, CF_4 or C_2F_6. After all this, the strategy was changed and attempts were made to fluorinate CF_3SeF_3 with F_2 or ClF to the corresponding CF_3SeF_5 or CF_3SeF_4Cl.

The successfully attempted reactions are:

$$CF_3SeF_3 + ClF \xrightarrow[10\ h]{-169°C\ -\ -78°C} CF_3SeF_4Cl \quad (20\%)$$

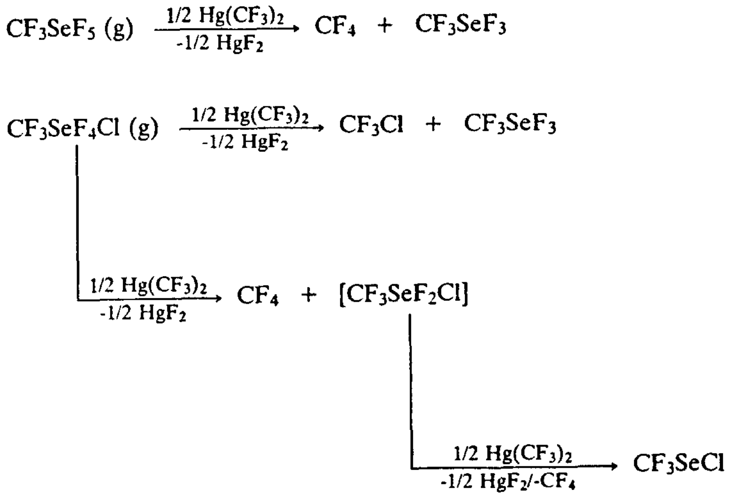
$$CF_3SeF_3 \cdot CsF + ClF \xrightarrow[10\ h]{-196°C\ -\ -78°C} CF_3SeF_4Cl \quad (5\text{-}10\%)$$

$$CF_3SeF_3 + F_2\,(l) \xrightarrow[20\ h]{-196°C} CF_3SeF_5 \quad (1\text{-}4\%)$$

$$CF_3SeF_3 + AgF_2 \xrightarrow[1\ mbar]{+65°C} CF_3SeF_5 \quad (3\%)$$

CF_3SeF_3 adds ClF at -196 to -78°C (10 h) to yield 20 % CF_3SeF_4Cl. In principle $CF_3SeF_3 \cdot CsF$ can also be used as a starting material in this reaction but the yields are lowered to 5 to 10 %. It was much more difficult to synthesize CF_3SeF_5 since normal fluorination gave only CF_4 and SeF_6. But with liquid F_2 very small amounts of CF_3SeF_5 are formed. A slightly improved method is found in the fluorination of CF_3SeF_3 with AgF_2 at 65°C and 1 mbar. Although the yields are again very low, this method is applicable since it can be carried out in a continous manner providing the wanted material on a gram scale.

Both substances are strong oxidizing agents, transmitting F_2 or ClF to other molecules; e.g. $Hg(CF_3)_2$ is converted to CF_4 or CF_3Cl and CF_3SeF_3. With CF_3SeF_4Cl a side reaction, presumably over a CF_3SeF_2Cl intermediate, yields CF_4 and CF_3SeCl as demonstrated below.



$$CF_3SeF_5\ (g) \xrightarrow[-1/2\ HgF_2]{1/2\ Hg(CF_3)_2} CF_4 + CF_3SeF_3$$

$$CF_3SeF_4Cl\ (g) \xrightarrow[-1/2\ HgF_2]{1/2\ Hg(CF_3)_2} CF_3Cl + CF_3SeF_3$$

$$CF_3SeF_4Cl\ (g) \xrightarrow[-1/2\ HgF_2]{1/2\ Hg(CF_3)_2} CF_4 + [CF_3SeF_2Cl]$$

$$[CF_3SeF_2Cl] \xrightarrow[-1/2\ HgF_2/-CF_4]{1/2\ Hg(CF_3)_2} CF_3SeCl$$

Both molecules are quite stable. Their thermolysis and photolysis are as follows:

Thermolysis:

$$CF_3SeF_5 \xrightarrow{70°C,\ 2\ h} CF_4 + SeF_4$$

$$CF_3SeF_4Cl \xrightarrow{70°C,\ 2h} CF_3Cl + SeF_4$$

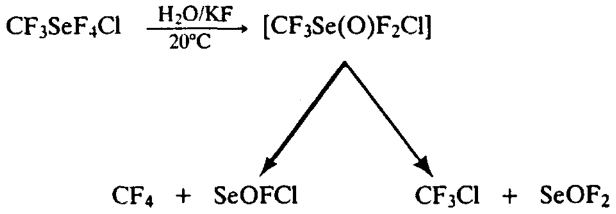
Photolysis:

$$CF_3SeF_4Cl \xrightarrow[laser]{488\ nm} [SeF_3Cl] + CF_4$$

$$[SeF_3Cl] \xrightarrow{SiO_2} SeOFCl$$

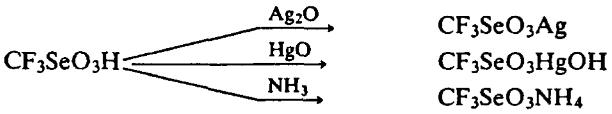
The most interesting reaction of course was hydrolysis, but it was rather disappointing since only decomposition products and no CF_3SeO_3H was observed.

$$CF_3SeF_5 \xrightarrow[20°C]{H_2O/KF} [CF_3Se(O)F_3] \longrightarrow CF_4 + SeOF_2$$



After two years of hard but unsuccessful work it was finally possible to synthesize CF_3SeO_3H and some of its salts. Surprisingly enough, the successful reaction is rather simple. It consists of the oxidation of CF_3SeO_2H with a saturated neutral $KMnO_4$ solution in H_2O at 20°C as shown:

$$CF_3SeO_2H \xrightarrow[-MnO_2]{KMnO_4} CF_3SeO_3K \xrightarrow[-KClO_4]{HClO_4/0°C} \boldsymbol{CF_3SeO_3H}$$



The primary product is the potassium salt, which forms with $HClO_4$ at 0°C the wanted acid, which so far is only stable in solution. Other salts are simply prepared by neutralisation with corresponding bases. Meanwhile, the barium salt was also synthesized and characterized. Attempts to isolate the acid from its aqueous solution by evaporating H_2O in vacuo showed that at concentration higher than 90 % decomposition takes place to the products given below.

$$2\,CF_3SeO_3H \xrightarrow[0°C]{conc.\ >90\%} CF_4 + COF_2 + 2\,SeO_2 + H_2O$$

$$2\,CF_3SeO_3^-M^+ \xrightarrow{\Delta} CF_4 + COF_2 + SeO_2 + M_2SeO_3$$

M =	(H)	Hg	Ag	NH_4	K
$T_{decomp.}$/°C	(0)	165	210	230	290
$\nu_{Se\text{-}O}$/cm^{-1} [Ra]	(860)	849	859	867	877

In a similar manner the salts decompose on heating at temperatures between 165 and 290°C [22].

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REFERENCES

1 A. Haas and H. Willner, Spectrochim. Acta 34A (1978) 541.

2 A. Haas and H. Willner, Z. anorg. allg. Chem. 462 (1980) 57.

3 H. Willner, Z. anorg. allg. Chem. 514 (1984) 171.

4 A. Haas and H. Willner, Spectrochim. Acta 35A (1979) 953.

5 A. Haas and H. Willner, Z. anorg. allg. Chem. 454 (1979) 17.

6 W. Gombler, A. Haas and H. Willner, Z. anorg. allg. Chem. 469 (1980) 135.

7 A. Haas and K. Tebbe, Z. Naturforsch. 39b (1984) 897.

8 A. Darmadi, A. Haas and M. Kaschani-Motlagh, Z. anorg. allg. Chem. 448 (1979) 35.

9 A. Haas and J. Mikolajczak, Chem. Ber. 114 (1981) 829.

10 A. Haas and A. Lopusinski, Chem. Ber. 114 (1981) 3176.

11 A. Haas, B. Koch and N. Welcman, Z. anorg. allg. Chem. 427 (1976) 114.

12 A. Darmadi, A. Haas and B. Koch, Z. Naturforsch. 35b (1980) 526.

13 J. Grobe and Duc Le Van, Angew. Chem. 96 (1984) 716; Angew. Chem. Int. Ed. 23 (1984) 710.

14 D. Christen, H. Oberhammer, W. Zeil, A. Haas and A. Darmadi, J. Mol. Struct. 66 (1980) 203.

15 T. Wehrung, H. Oberhammer, A. Haas, B. Koch and N. Welcman, J. Mol. Struct. 35 (1976) 253.

16 H. Oberhammer, A. Darmadi and A. Haas, unpublished results.

17 F. Fockenberg and A. Haas, Z. Naturforsch. in press.

18 H. Hartl, P. Huppmann, D. Lentz, K. Seppelt, Inorg. Chem. 22 (1983) 2183.

19 N. Y. Derkach, G. G. Baraschenkov and E. S. Levckenko, Zhr. Org. Khim. 15 (1979) 1547; J. Org. Chem. USSR 15 (1979) 1381.

20 C. Lau and L. Passmore, J. Fluorine Chem. 7 (1976) 261.

21 J. W. Dale, H. J. Emelêus and R. N. Haszeldine, J. Chem. Soc. 1958, 2939.

22 A. Haas and H.-U. Weiler, Chem. Ber. 118 (1985) 943.