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SOME NEW PERFLUOROALKYL DERIVATIVES OF SeF_4 and SeF_6

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To Professor George H. Cady on his 70th birthday.

SUMMARY

$(CF_3)_2SeF_2$ and $(C_2F_5)_2SeF_2$ are prepared by the reactions of the corresponding bis(perfluoroalkyl) monoselenide with chlorine monofluoride, and $C_2F_5SeF_3$ by reacting bis(perfluoroethyl) diselenide with ClF. Trans $C_2F_5SeClF_4$ is made by the reactions of either $C_2F_5SeF_3$, $CsF.C_2F_5SeF_3$, or $(C_2F_5)_2SeF_2$ with chlorine monofluoride, and $C_2F_5SeF_5$ is produced by direct fluorination of $CsF.C_2F_5SeF_3$. $(C_2F_5)_2SeF_2$ and $C_2F_5SeF_3$ form the adducts $(C_2F_5)_2SeF_2.AsF_5$ (or SbF_5), $C_2F_5SeF_3.SbF_5$ and $CsF.C_2F_5SeF_3$.

The ^{19}F n.m.r. and vibrational spectra of the neutral perfluoroalkyl selenium(IV) derivatives have been recorded, and the results show their structures to be based on a trigonal bipyramid with the perfluoroalkyl group(s) preferentially occupying equatorial positions. The vibrational spectrum of $CsF.C_2F_5SeF_3$ is consistent with an ionic formulation, and the spectra of the pentafluoride adducts suggest a substantial ionic contribution, with anion-cation interaction.

The trans configuration of $C_2F_5SeClF_4$ is consistent with its vibrational spectrum and is confirmed by the ^{19}F n.m.r study. The structure of $C_2F_5SeF_5$ is deduced from its ^{19}F n.m.r spectrum.

INTRODUCTION

Perfluoroalkyl derivatives of sulphur tetrafluoride and hexafluoride are well known [1-5]. Chlorine monofluoride has been shown to act as a mild fluorinating agent in a number of reactions. In particular, it has been successfully used in the preparation of perfluoroalkyl sulphur(IV) and (VI) derivatives [6,7], however, analogous selenium derivatives have not been prepared [2,3,8-10]. Various alkyl and aryl selenium(IV) halides, where the halides are chlorine, bromine and iodine, are well known [9,10]. The structure of these compounds can take a variety of forms and have been the subject of much investigation [11-18]. Bis(alkyl) and bis(aryl) selenium difluorides have been reported [19] and the vibrational spectrum of bis(perfluoromethyl) selenium difluoride investigated [20]. A preliminary report of some aryl selenium trifluoride has been given [21]. Organic derivatives of selenium hexafluoride have not been prepared as far as we are aware. We wish to report the preparation and characterization by spectroscopic methods of some perfluoroalkyl derivatives of SeF_4 and SeF_6 by using chlorine monofluoride as a mild oxidizing agent, a preliminary account of part of this work has been reported [22-3].

EXPERIMENTAL

Apparatus

Volatile materials were manipulated in a Monel vacuum line equipped with stainless steel valves (Whitey 1KS4) and Swagelok compression fittings or a Pyrex glass vacuum line equipped with "Rotaflo" valves. Solids and involatile compounds at room temperature were transferred in a Vacuum Atmospheres Corp. Dri-Lab fitted with a Dri-train (HE-493). Reaction vessels were constructed from Kel-F tubing (1/2" O.D.; 5/16" I.D.) connected to a Whitey valve via a brass reducing Swagelok junction; or glass tubing, vol. 30 c.c. equipped with "Rotaflo" valves. High pressure reactions were carried out in Monel vessel, vol. 30 c.c. equipped with removable lids and Teflon gaskets. In general, all reactions were carried out in Kel-F vessels unless otherwise specified.

Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer in the range 4000-250 cm^{-1}. The instrument was calibrated by comparison with a standard polystyrene sheet. Gaseous spectra were obtained using a stainless steel 10 cm cell equipped with AgCl windows. Spectra of solids were obtained as fine powders between silver chloride plates.

Raman spectra were recorded on a Spex Ramalab spectrometer using a Spectra Physics 2W Ar-Kr ion laser as a source with exciting line at 5145Å. The spectrometer was calibrated against the known bands of carbon tetrachloride and indene, and was believed to have an accuracy ±3 cm^{-1} for those of sharp bands, and ±8 cm^{-1} for the broad bands. The slit width was 4 cm^{-1} for both solid and liquid samples unless otherwise specified. Samples were sealed either in glass capillary or in FEP thin walled tubing of O.D. 4 mm. Polarization measurements were carried out by means of an Ednalite polarization rotator.

^{19}F n.m.r. spectra were recorded using a Varian Associate HA-60 spectrometer operating at 56.4 Mc. Trichlorofluoromethane was used as an internal standard. Samples were sealed either in standard size thin wall n.m.r. tubes or in FEP thin walled tubing.

Preparative chromatography was carried out by means of a model 2465T Dohrmann Envirotech gas chromatograph equipped with a manual collection unit using a 1/4" X 10' stainless steel column containing 10% Kel-F wax (Applied Science Laboratories) on 45/60 mesh Chromasorb W (Applied Science Laboratories). Programs were run isothermally at 80°C with a helium gas flow rate of about 33 ml/min.

Mass spectra were obtained using a Hitachi Perkin Elmer RMU-6D mass spectrometer routinely run at 70 e.v. by the indirect introduction port.

Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany.

Chemicals

Selenium (Fisher Scientific Co.), silver oxide (Anachemia Chemical Ltd.), pentafluoropropionic acid and trifluoromethyl hypofluorite (P.C.R.), tetrafluoroethylene (Columbia Organic Chemicals), trifluoroacetic acid (Aldrich Chemical Co.), arsenic pentafluoride and cesium fluoride (Ozark, Mahoning Co.) and fluorine (Matheson Co.) were directly used without purification.

Chlorine monofluoride (Ozark, Mahoning Co.) was purified by vacuum distillation at room temperature.

Bis(pentafluoroethyl) monoselenide and bis(trifluoromethy monoselenide were prepared by the reactions of selenium powder with corresponding perfluoroalkyl silver salts [24]. The bis(pentafluoroethyl) monoselenide contained about 5% of trifluoromethyl pentafluoroethyl monoselenide. Both monoselenides were stored over P_2O_5 before use. Bis(pentafluoroethyl) diselenide was prepared by the reaction of tetrafluoroethylene with octaselenium bis(hexafluoroarsenate) [25].

Preparation and Reactions

(i) Preparation of $(CF_3)_2SeF_2$.

In a typical reaction, ClF (5.88 mmole) was reacted with $(CF_3)_2Se$ (2.72 mmole) at room temperature for about 1 hr. The product was a yellow liquid and was separated with the vessel held at -78°C. The infrared spectrum of the volatile fraction at -78°C showed the presence of unreacted ClF and some fluorocarbon bands. Chlorine was probably present; the involatile fraction was a colorless liquid at room temperature correspondi 2.67 mmole of $(CF_3)_2SeF_2$ (98% yield). The mass spectrum of this compound contained peaks at M/e 237*, $(CF_3)_2SeF^+$ (4); 218, $(CF_3)_2Se^+$ (5); 187, $CF_3SeF_2^+$ (4); 168, CF_3SeF^+ (9); 149, CF_3Se^+ (25); 130, CF_2Se^+ (17); 99, SeF^+ (10); 80, Se^+ (12); 69, CF_3^+ (100); 50, CF_2^+ (23); 31, CF^+ (15).

*Based on Se^{80}, peaks attributable to the other selenium isotopes were also observed.

(ii) Preparation of $(C_2F_2)_2SeF_2$.

$(C_2F_2)_2SeF_2$ is prepared by the reaction of $(C_2F_2)_2Se$ with ClF either at -78°C or room temperature. ClF (4.6 mmole) was reacted with $(C_2F_5)_2Se$ (2.18 mmole) at -78°C for about 30 min. giving a yellow liquid product. The volatile materials were removed from the product (held at -45°C) by distillation and were shown to contain traces of fluorocarbons and $(C_2F_5)_2Se$ Chlorine was probably also a product. The involatile product was a clear liquid at ambient temperature corresponding 2.19 mmole of $(C_2F_5)_2SeF_2$ (100% yield). The ^{19}F n.m.r. spectrum of this liquid indicated that it contained about 5% $CF_3SeF_2CF_2CF_3$. A pure sample of $(C_2F_5)_2SeF_2$ was obtained by preparative v.p.c.

Reactants in different ratios, reaction vessels and temperatures gave the same product (Table 1). The chemical analysis of this compound is given in Table 3. The mass spectrum showed peaks at M/e 337, $(C_2F_5)_2SeF^+$ (1); 318, $(C_2F_5)_2Se^+$ (4.0); 299, $C_2F_5SeC_2F_4{}^+$ (<1); 249, $C_2F_5SeCF_2{}^+$ (1); 237, $C_2F_5SeF_2{}^+$ (1); 218, $C_2F_5SeF^+$ (2); 199, $C_2F_5Se^+$ (5); 180, $C_2F_4Se^+$ (20); 161, $C_2F_3Se^+$ (6); 130, CF_2Se^+ (11); 119, $C_2F_5{}^+$ (72); 111, $CFSe^+$ (19); 100, $C_2F_4{}^+$ (4.0); 80, Se^+ (6); 69, $CF_3{}^+$ (100); 50, $CF_2{}^+$ (6); 31, CF^+ (23).

Table 1.

Preparations of $(C_2F_5)_2SeF_2$

$(C_2F_5)_2Se$:ClF	Conditions	$(C_2F_5)_2SeF_2$[a]
2.18[c]:4.6[c]	r.t. for 30 min.	2.19[c] ca.[a] 100%[b]
1.36:2.8	-78°C overnight	1.37 ca. 100%
1.17:5.56	-78°C 2 days	1.15 ca. 98% + ClF
2.93:5.92	r.t. overnight	2.88 ca. 99%
2.36:7.22	r.t. 30 min.	2.31 ca. 98%

[a] The product contained about 5% $C_2F_5SeF_2CF_3$.
[b] Yield.
[c] mmole.

(iii) Preparation of $C_2F_5SeF_3$.

In a typical experiment ClF (46 mmole) in small aliquots was reacted with $(C_2F_5)_2Se_2$ (7.6 mmole) in a glass vessel. The mixture was held at -130°C for 15 min.; then at -78°C for 20 min. and finally warmed up to room temperature in order to let any solid melt prior to the next addition of ClF. (Caution! If too much of ClF is used each time, a violent reaction occurs.) The yellow diselenide turned red; later orange and finally slightly yellow when the full amount of ClF has been used. The product (held at -22°C for 3 hr.) was separated by distillation and the volatile fraction was shown by its infrared spectrum to contain small amounts of C_2F_6, SiF_4 and a trace of fluorocarbons. The vapour pressure measurements and colour of this fraction at various temperatures were consistent with the presence of chlorine. The involatile fraction was a white solid at -22°C, which melted to a clear liquid at room temperature, corresponding at 15.2 mmole of $C_2F_5SeF_3$ (100% yield).

Similar results were obtained in other preparations (Table 2). The chemical analysis of this compound is given in Table 3.

Table 2.
Preparations of $C_2F_5SeF_3$

$(C_2F_5)_2Se_2$:ClF	Reaction vessel	$C_2F_5SeF_3$
$7.6^a:46^a$	glass tube	15.2^a, ca. ^{b}100%
10.36:77.5	glass tube	20.7, ca. 100%
2.25:17.8	Kel-F vessel, vol.13c.c.	4.9*
17.62:112.8	glass bulb, vol.60c.c.	35.4, ca. 100%

*Based on the weight, assuming pure $C_2F_5SeF_3$. The liquid was yellow and probably contained elemental chlorine.
[a] mmole [b] yield

(iv) Reaction of $(C_2F_5)_2SeF_2$ with CsF.

Cesium fluoride did not react detectably with $(C_2F_5)_2SeF_2$ at 80°C for 2 hours. $(C_2F_5)_2SeF_2$ (1.66 mmole) was condensed onto powdered CsF (1.25 mmole) and the mixture held at 120°C for 90 min. with bubbling. The product was then cooled to room temperature. The volatile product was 0.52 g. clear liquid at room temperature which was identified by its infrared spectrum as mainly $(C_2F_5)_2SeF_2$ with traces of C_2F_6. There was 0.26 g. of solid remaining in the vessel, the infrared spectrum of this solid showed absorptions attributable to $CsF.C_2F_5SeF_3$.

(v) Preparation of $(C_2F_5)_2SeF_2.AsF_5$ and $(C_2F_5)_2SeF_2.SbF_5$.

$(C_2F_5)_2SeF_2$ (1.12 mmole) was reacted with excess AsF_5 (1.53 mmole) at room temperature for 30 min. The product was a white solid. The unreacted AsF_5 was removed by pumping the product at ambient temperature leaving 1.06 mmole of $(C_2F_5)_2SeF_2.AsF_5$ (about 95% yield).

Excess $(C_2F_5)_2SeF_2$ (1.15 mmole) was reacted with SbF_5 (0.78 mmole) at room temperature for 30 min. The product was a white solid. The unreacted $(C_2F_5)_2SeF_2$ was removed by distillation at room temperature leaving 0.77 mmole of $(C_2F_5)_2SeF_2.SbF_5$ (99% yield).

(vi) Preparation of $CsF.C_2F_5SeF_3$.

$C_2F_5SeF_3$ (2 mmole) was condensed onto ground powdered CsF (1.9 mmole). The mixture was held at ca. 50°C for 1 hr. and a new white solid formed. Trace volatile materials were shown by i.r. to contain $(C_2F_5)_2Se$, and were removed by pumping at room temperature, $CsF.C_2F_5SeF_3$ (1.9 mmole) remaining in the vessel (100% yield). The chemical analysis of this compound is given in Table 3.

(vii) Preparation of $C_2F_5SeF_3.SbF_5$.

Excess $C_2F_5SeF_3$ (4.78 mmole) was reacted with SbF_5 (3.35 mmole) at room temperature with occasional shaking for 2 hr. The product was a white solid. Traces volatile materials were identified by infrared as SiF_4 and fluorocarbons, and were removed by pumping the product at room temperature to constant weight. The solid product corresponded to 3.58 mmole of $C_2F_5SeF_3.SbF_5$. The chemical analysis of this compound is given in Table 3. and suggests the compound was either not completely pure or suffered some decomposition before analysis.

(viii) Preparation of trans $C_2F_5SeClF_4$.

(a). By the reaction of $C_2F_5SeF_3$ with ClF

Chlorine monofluoride (2.75 mmole) was reacted with $C_2F_5SeF_3$ (2.36 mmole) at room temperature overnight. The product was a yellow liquid. The fraction volatile at -78°C was found by infrared to contain C_2F_6, C_2F_5Cl and trace $FClO_2$. Chlorine was probably present; the fraction between -78°C and -22°C consisted of 1.58 mmole trans $C_2F_5SeClF_4$; and the fraction between -22°C and room temperature was 0.55 mmole of unreacted $C_2F_5SeF_3$.

An excess of chlorine monofluoride and longer reaction times resulted in different products. When $C_2F_5SeF_3$ (2.78 mmole) was reacted with ClF (6.1 mmole) at room temperature for 4 days, the product included mainly $SeClF_5$ in addition to C_2F_5Cl and C_2F_6; $C_2F_5SeClF_4$ was not detected.

(b). By the reaction of $CsF.C_2F_5SeF_3$ with ClF

Chlorine monofluoride (16 mmole) was condensed onto ground powdered $CsF.C_2F_5SeF_3$ (2.43 mmole) at -78°C overnight. The volatile products at -78°C were found by infrared to contain unreacted ClF, C_2F_6 and trace of trans $C_2F_5SeClF_4$. The product vola between -78°C and room temperature was a colorless liquid corresponding to 1.75 mmole of trans $C_2F_5SeClF_4$ (ca. 70% yield). An X-ray powder diffraction picture showed the remaining solid to be $Cs^+ClF_2^-$, an authentic sample was prepared by the method given in reference 26.

The chemical analysis of this compound is given in Table 3.

(c). By the reaction of $(C_2F_5)_2SeF_2$ with ClF (refer to reaction (xii)).

Table 3.
Analytical data for perfluoroethyl selenium derivatives.

Compound		C	F	Se	Cs	Sb	Cl	Total
$(C_2F_5)_2SeF_2$	(a)	13.52	64.23	22.25				100
	(b)	13.30	63.96	21.94				99.20
$C_2F_5SeF_3$	(a)	9.41	59.6	30.97				100
	(b)	9.28	59.19	30.59				99.06
$CsF.C_2F_5SeF_3$	(a)	5.90	42.03	19.41	32.67			100
	(b)	5.94	41.77	19.24	32.26			99.21
$C_2F_5SeF_3.SbF_5$	(a)	5.09	52.36	16.74		25.81		100
	(b)	3.04	49.12	18.58		28.63		99.37
$C_2F_5SeClF_4$	(a)	7.76	55.26	25.52			11.46	100
	(b)	7.63	55.27	25.24			11.33	99.47

(a) Cal. %
(b) Found %

(ix) Preparation of $C_2F_5SeF_5$.

Fluorine (2.1 mmole) was added (in small aliquots) to ground powdered $CsF.C_2F_5SeF_3$ (0.52 mmole). The mixture was held at -196°C for 20 minutes then at -78°C for 30 minutes prior to next addition of fluorine. The unreacted fluorine was removed by pumping the product at -196°C via a soda-lime trap. The volatile product at room temperature was distilled out from the reaction vessel and shown by infrared and ^{19}F n.m.r. spectra to contain CF_4, C_2F_6, SeF_6 and $C_2F_5SeF_5$. The remaining solid was unidentified.

(x) Reaction of trans $C_2F_5SeClF_4$ with Hg.

$C_2F_5SeClF_4$ (0.9 mmole) was condensed onto Hg (1.25 mmole) at room temperature for 2 hours. Bubbles were evolved and some solid formed. The volatile products were found by their infrared and ^{19}F n.m.r. spectra to contain mainly $C_2F_5SeF_3$ and small amount of $C_2F_5SeClF_4$, the solid products were probably mercuric chloride and fluoride.

(xi) Reaction of trans $C_2F_5SeClF_4$ with ClF at 90°C.

Chlorine monofluoride (2.75 mmole) was reacted with $C_2F_5SeClF_4$ (0.65 mmole) at 90°C overnight. Both infrared and ^{19}F n.m.r. spectra of the products showed it to contain C_2F_6, C_2F_5Cl and $SeClF_5$.

(xii) Attempts to prepare $(CF_3)_2SeF_4$ and $(C_2F_5)_2SeF_4$.

Reactions attempting to prepare $(R_f)_2SeF_4$ (R_f = CF_3, C_2F_5) are listed in Table 4. Neither $(CF_3)_2SeF_4$ nor $(C_2F_5)_2SeF_4$ were detected.

Table 4. Attempted preparations of $(R_f)_2SeF_4$ (R_f = CF_3, C_2F_5)

Reactant	Conditions[b]	Product
$(CF_3)_2Se$ (3.7)[a] ClF (19.8)	overnight (A)	ClF, CF_3Cl, $(CF_3)_2SeF_2$ (3.53)
$(CF_3)_2SeF_2$ (1.4) ClF (3.7)	5 days (B)	$(CF_3)_2SeF_2$ mainly $SeClF_5$*, CF_4 CF_3Cl
$(CF_3)_2SeF_2$ (0.9) ClF (14.3)	3 days (A)	ClF, mainly $SeClF_5$, CF_4
$(C_2F_5)_2SeF_2$ (2.9) ClF (5.9)	15 hours (A)	ClF, $(C_2F_5)_2SeF_2$, (2.8) traces of fluorocarbons
$(C_2F_5)_2SeF_2$ (1.5) ClF (5.5)	80°C 2 days (A)	ClF, $(C_2F_5)_2SeF_2$ mainly C_2F_5Se C_2F_6 and C_2F_5Cl
$(C_2F_5)_2SeF_2$ (1.3) ClF (16.3)	2 days (A)	ClF, $(C_2F_5)_2SeF_2$, mainly C_2F_5 C_2F_6 and C_2F_5Cl
$(C_2F_5)_2SeF_2$ (0.9) CF_3OF (1.1)	3 hours (B)	No reaction
$(C_2F_5)_2SeF_2$ (0.9) CF_3OF (1.2)	70°C 2 hrs. (B)	$(C_2F_5)_2SeF_2$, C_2F_6, COF_2, SeF_6 and unidentified

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* $SeClF_5$ is characterized by its ^{19}F n.m.r. which is reported i reference [27].

A. Monel vessel B. Kel-F vessel

a mmole given in bracket.

b carried out at room temperature unles wise stated.

RESULTS AND DISCUSSION

Preparations

Bis(perfluoroethyl) monoselenide and bis(perfluoromethyl) monoselenide both react with chlorine monofluoride in a 1:2 rati at -78°C or at room temperature to give the corresponding difluoride in essentially quantitative yield according to the equation (1).

$$(1)\quad (R_f)_2Se + 2ClF \rightarrow (R_f)_2SeF_2 + Cl_2$$
$$R_f = CF_3,\ C_2F_5$$

Traces of $CF_3SeC_2F_5$ in $(C_2F_5)_2Se$ starting material yielded corresponding amounts of $CF_3SeF_2C_2F_5$ product. A ^{19}F n.m.r. spectrum of a 1:1 mixture of $(C_2F_5)_2Se$ and ClF at room temperature gave no evidence for an intermediate $(C_2F_5)_2SeClF$.

Bis(perfluoroethyl) diselenide reacts with chlorine monofluoride in about 1:6 ratio at -78°C to give perfluoroethyl selenium trifluoride essentially quantitatively according to equation (2). The reaction was much more vigorous than the corresponding reaction of chlorine monofluoride and bis(perfluoroalkyl) monoselenide, and was carefully controlled.

$$(2)\quad (C_2F_5)_2Se_2 + 6ClF \rightarrow 2C_2F_5SeF_3 + 3Cl_2$$

Presumably the selenium-selenium bond is cleaved to yield C_2F_5SeCl [consistent with observations that a red intermediate is formed during the reaction], and C_2F_5SeF. The monofluoride may disproportionate to the diselenide and the trifluoride, by analogy with the sulphur analogue [28,29]. Perfluoroethyl selenium chloride may be further oxidized by chlorine monofluoride to finally yield perfluoroethyl selenium trifluoride.

Trans perfluoroethyl selenium chloride tetrafluoride may be prepared by three routes. (a) The reaction of chlorine monofluoride in a slight excess with perfluoroethyl selenium trifluoride at room temperature. The reaction went in about 90% yield according to equation (3).

$$(3)\quad C_2F_5SeF_3 + ClF \xrightarrow[\text{overnight}]{r.t.} C_2F_5SeClF_4$$

Presumably this reaction proceeds by direct addition of ClF. When the reaction was carried out with an excess of ClF for four days, selenium chloride pentafluoride is formed, essentially quantitatively (equation 4).

(4) $C_2F_5SeClF_4 + ClF \xrightarrow{r.t.} SeClF_5 + C_2F_5Cl$

The reaction goes to completion in a shorter time at higher temperatures (e.g. 90°C). Selenium chloride pentafluoride has been previously reported [27,30]. (b) Trans $C_2F_5SeClF_4$ is also prepared by the reaction of $CsF.C_2F_5SeF_3$ with chlorine monofluoride at -78°C, in about 70% yield according to (5).

(5) $CsF.C_2F_5SeF_3 + 2ClF \xrightarrow{-78°C}$ Trans $C_2F_5SeClF_4 + Cs^+ClF_2^-$

This may be a displacement reaction and is perhaps the best way to prepare the compound since unreacted chlorine monofluoride is readily removed at -78°C and other products are involatile solids at ambient temperature. (c) The reaction of bis(perfluoroethyl) selenium difluoride with chlorine monofluoride can also produce trans $C_2F_5SeClF_4$. Bis(perfluoroethyl) selenium difluoride did not react with ClF in a 1:2 ratio overnight, but the reaction occurred slowly with ClF in a 1:12.7 ratio at room temperature for 2 days. Unreacted starting material was recovered in this reaction. A similar result was obtained when $(C_2F_5)_2SeF_2$ was reacted with ClF in a 1:3.8 ratio for 2 days at 80°C and in a 1:2.9 ratio in the presence of cesium fluoride overnight. It is clear that bis(perfluoroethyl) selenium difluoride is much less reactive toward chlorine monofluoride than perfluoroethyl selenium trifluoride. Reaction of $(C_2F_5)_2SeF_2$ may proceed by addition of ClF across a carbon-selenium bond with formation of $C_2F_5SeF_3$ and C_2F_5Cl, or by an oxidative addition with formation of $(C_2F_5)_2SeClF_3$ which may disproportionate, decompose, or further react with ClF to give trans $C_2F_5SeClF_4$ and other products. The analogous reaction of bis(perfluoroalkyl) sulphides led to the formation of bis(perfluoroalkyl) sulphur tetrafluoride [31]. We have been unable to detect the selenium analogues in any of our preparations. Selenium-carbon bonds may be expected to be weaker than the corresponding sulphur-carbon bonds, and selenium(IV) seems to be the preferred oxidation state of the element [3]. Thus it is not unexpected that the selenium analogues of cis and trans $(R_f)_2SF_4$ should be more difficult to prepare.

Perfluoroethyl selenium pentafluoride was formed with SeF_6, C_2F_6, CF_4 by the fluorination of $CsF.C_2F_5SeF_3$ at -78°C. This material was not isolated but characterized by ^{19}F n.m.r. spectroscopy.

Properties

$(C_2F_5)_2SeF_2$, $(CF_3)_2SeF_2$, $(C_2F_5)SeF_3$ and Trans $C_2F_5SeClF_4$ are colourless liquids at room temperature with vapour pressures of ca. 25, 35, 10 and 75 torr at room temperature. All are stable at room temperature in Kel-F vessels over periods of months. The trifluoride is more reactive than the difluoride towards glass and meaningful mass spectra were not obtained. The perfluoroethyl trifluoride, like selenium tetrafluoride, reacts with both as a fluoride ion donor and acceptor and forms 1:1 complexes with cesium fluoride and antimony pentafluoride quantitatively according to equation (6) and (7).

(6) $CsF + C_2F_5SeF_3 \xrightarrow{r.t.} CsF.C_2F_5SeF_3$

(7) $SbF_5 + C_2F_5SeF_3 \xrightarrow{r.t.} C_2F_5SeF_3.SbF_5$

Unlike perfluoroethyl selenium trifluoride, bis(perfluoroethyl) selenium difluoride does not form a complex with cesium fluoride; however 1:1 adducts are formed with arsenic and antimony pentafluoride quantitatively according to equation (8). These adducts decompose at room

(8) $(C_2F_5)_2SeF_2 + MF_5 \rightarrow (C_2F_5)_2SeF_2.MF_5$ (M = As, Sb)

temperature like the similar related adduct $(C_6H_5)_2SeCl_2.BCl_3$ [32]. Boron trifluoride has also been reported to cause decomposition of $(C_6H_5)_2SeF_2$ [33].

Trans $C_2F_5SeClF_4$ is reduced by elemental mercury to $C_2F_5SeF_3$ at room temperature.

^{19}F n.m.r. Spectra

The ^{19}F n.m.r. spectra data for the various neutral compounds prepared in this work are given in Table 5. Chemical shifts are compared with the analogous sulphur compounds in Table 6, and coupling constants compared in Table 7, perfluoroethyl selenium trifluoride is not included as the corresponding sulphur analogue has not been prepared.

The fluorine chemical shift found for $(CF_3)_2Se$ is comparable with that recently reported by Marsden [37]. High resolution spectra were obtained for $CF_3SeC_2F_5$, $(C_2F_5)_2SeF_2$, $(CF_3)_2SeF_2$, Trans $C_2F_5SeClF_4$ and $C_2F_5SeF_5$. The n.m.r. data establishes the configuration of the latter two compounds unambiguously and the Se^{77}-F couplings are in the range for that expected for Se^{77}(VI)-F. The spectrum of $C_2F_5SeF_5$ closely resembles that of various pentafluorosulphur containing compounds [38-40] and $SeClF_5$ [27] despite the further couplings with the C_2F_5 group. The J_{AB} coupling constant 184 ± 5 Hz in the AB_4 part of the spectrum was deduced by application of the equation given in reference 38.

Table 5. ^{19}F n.m.r. data of perfluoroalkyl selenium derivatives

Compound	Chemical shifts(p.p.m.)	Coupling constant(Hz)
$(CF_3)_2Se$	$^{\delta}CF_3 = 31.6$	
$CF_3SeC_2F_5$	$\delta CF_3Se = 29.9(3)$(t.q.)	$^{J}CF_3Se\text{-}CF_2 = 9.19$
	$\delta CF_2 = 88.31(2)$(q.q.)	$^{J}CF_3Se\text{-}CF_3 = 3.06$
	$\delta CF_3C = 84.7(3)$(t.q.)	$^{J}CF_3\text{-}CF_2 = 3.45$
$(CF_3)_2SeF_2$	$\delta CF_3 = 53.23(3)$(t)	$^{J}CF_3\text{-}SeF_2 = 12.99$
	$\delta SeF_2 = 68.84(1)$(s)	$^{J}Se^{77}\text{-}F = 377 \pm 10$

Table 5. (continued)

Compound	Chemical shift(p.p.m.)	Coupling constant(Hz)
$C_2F_5SeF_2CF_3$	δCF_3 = 51.53(3)	
	δSeF_2 = 65.56(2)	
	δCF_2 = 98.19(2)	
	δCF_3C = 80.24(3)	
$(C_2F_5)_2SeF_2$	δCF_3 = 79.5(3)(t)	$^{J}CF_3$-CF_2 = 0
	δCF_2 = 96.7(2)(t?)	$^{J}CF_3$-SeF_2 = 8.1
	δSeF_2 = 63.5(1)(p.s.)	$^{J}CF_2$-SeF_2 = 16.23
$C_2F_5SeF_3$	δCF_3 = 78.8(3)	
	δCF_2 = 103.5(2)	
	δSeF_3 = 25.9(3)	
$C_2F_5SeClF_4$	δCF_3 = 79.4(3)(t.p.)	$^{J}CF_3$-CF_2 = 1.50
	δCF_2 = 87.5(2)(q.p.)	$^{J}CF_3$-$SeF_{4(eq)}$ = 7.40
	$\delta SeF_{4(eq)}$ = 102.4(4)	$^{J}CF_2$-$SeF_{4(eq)}$ = 14.7
	(t.q.)	$^{J}Se^{77}$-$F_{(eq)}$ = 1192
$C_2F_5SeF_5$	δCF_3 = 79.64(3)(t.p.)	$^{J}CF_3$-CF_2 = 1.32
	δCF_2 = 86.75(2)(d.q.p.)	$^{J}CF_3$-$SeF_{4(eq)}$ = 6.89
	$\delta SeF_{4(eq)}$ = -36.23(4)	$^{J}CF_2$-$SeF_{4(eq)}$ = 13.52
	$\delta SeF_{(ax)}$ = 64.41(1)	$^{J}CF_3$-$SeF_{(ax)}$ = 0
	$\delta F_{ax.}$-$F_{4(eq)}$ = 1590	$^{J}CF_2$-$SeF_{(ax)}$ = 2.74
	±5(Hz)	$^{J}SeF_{ax.}$-$SeF_{4(eq)}$ = 183.7 ± 5
		$^{J}Se^{77}$-$F_{(eq)}$ = 1285.

N.B. Chemical shifts are relative to CCl_3F

Figures in bracket stand for areas under the peak

d=doublet, t=triplet, q=quartet, p=pentet and s=septet.

Table 6. Comparison of Chemical Shifts[a] of Some Perfluoroalkyl Derivatives of Sulphur and Selenium

Compound	CF_3	SF_2	SF_4	Ref.	Compound	CF_3	SeF_2	SeF_4	Ref.
$(CF_3)_2S$	38.6			34	$(CF_3)_2Se$	31.6			this work
$(CF_3)_2S_2$	46.9			34	$(CF_3)_2Se_2$	38.1			34
$(CF_3)_2SF_2$	58.0	14.2		6	$(CF_3)_2SeF_2$	53.2	68.8		this work

Compound	CF_3S	CF_3C	CF_2	SF_2	Ref.	Compound	CF_3Se	CF_3C	CF_2	SeF_2	Ref.
$CF_3SCF_2CF_3$	36.2	84.6	90.4		6	$CF_3SeC_2F_5$	29.9	84.7	88.3		this work
$CF_3SF_2C_2F_5$	55.8	80.2	100.7	13.2	35	$CF_3SeF_2C_2F_5$	51.5	80.2	98.2	65.6	this work

Compound	CF_3	CF_2	SF_2	$SF_{4eq.}$	$SF_{ax.}$	Ref.	Compound	CF_3	CF_2	SeF_2	$SeF_{4eq.}$	$SeF_{ax.}$	Ref.
$(C_2F_5)_2S_2$	85.4	97.2				28	$(C_2F_5)_2Se_2$	82.9	90.8				36
$(C_2F_5)_2SF_2$	80.5	98.9	11.2			6	$(C_2F_5)_2SeF_2$	79.5	96.7	63.5			this work
$C_2F_5SClF_4$[b]	81.1	98.8		-109.5		7	$C_2F_5SeClF_4$[b]	79.4	87.5		-102.4		this work
$C_2F_5SF_5$	81.5	99.8		-43.1	-62.5	7	$C_2F_5SeF_5$	79.6	86.7		- 36.2	-64.1	this work

---

[a] chemical shifts are in p.p.m. relative to CCl_3F.

[b]

Table 7. Comparison of coupling constants of some perfluoroalkyl derivatives of sulphur and selenium

Compound	$J_{CF_3M\text{-}CF_2}$		$J_{CF_3\text{-}CF_2}$	$J_{CF_3M\text{-}CF_3C}$		Reference
$CF_3SCF_2CF_3$	9.9		2.85	2.6		6
$CF_3SeCF_2CF_3$	9.19		3.45	3.06		this work
Compound			$J_{CF_3\text{-}MF_2}$			Reference
$(CF_3)_2SF_2$			19.5			6
$(CF_3)_2SeF_2$			12.99			this work
Compound	$J_{CF_2\text{-}MF_2}$		$J_{CF_3\text{-}CF_2}$	$J_{CF_3\text{-}MF_2}$		Reference
$(C_2F_5)_2SF_2$	19.0		9.6			6
$(C_2F_5)_2SeF_2$	16.23			8.1		this work
Compound	$J_{CF_3\text{-}CF_2}$		$J_{CF_3\text{-}MF_4}$	$J_{CF_2\text{-}MF_4}$		Reference
$C_2F_5SClF_4$[b]	0.6		8.8	14.3		7
$C_2F_5SeClF_4$[b]	1.5		7.4	14.7		this work
Compound	$J_{CF_3\text{-}CF_2}$	$J_{CF_3\text{-}MF_{4(eq)}}$	$J_{CF_2\text{-}MF_{4(eq)}}$	$J_{CF_2\text{-}MF_{(ax.)}}$	$J_{A\text{-}B}$	Reference
$C_2F_5SF_5$		9.0	14.0	4.7	146	7
$C_2F_5SeF_5$	1.32	6.89	13.52	2.74	184	this work

[a] Coupling constants are in Hz [b] Trans isomer

This value appears to be the lowest coupling constant that has been reported for an SeF_5 group in a variety of compounds [41]. It is noted that the J_{AB} values for the perfluoroalkyls of SF_5 are lower than the other sulphur analoguous of the compounds reported in reference 41.

The high resolution spectrum of $(CF_3)_2SeF_2$ appeared to be first order and a Se^{77}-F coupling constant of 377 ± 10 Hz was obtained, indicating that if intermolecular fluorine excha occurred, it was not rapid. A similar coupling constant was observed by Wynne for some bis(alkyl) selenium difluorides [19]. The high resolution spectrum of $(CF_3)(C_2F_5)SeF_2$ was poorly resolved and no interpretation was made. The high resolution spectrum of $(C_2F_5)_2SeF_2$ appeared to be essentially first order but had some features that suggested second order effects were operative although the apparent data is reported in the tables. This spectrum is being further investigated. The related compound $(CF_3)(C_2F_5)SF_2$ has been analysed by Sauer et al as a $AA'XX'Y_3Z_3$ system, and $(C_2F_5)_2SF_2$ is reported to have a complex spectrum [35]. The n.m.r. data are not inconsistent with an axial disposition of the fluorine in the $(R_f)_2SeF_2$ compounds, but more direct evidence is given below from vibrational spectra.

Perfluoroethyl selenium trifluoride did not give a high resolution spectrum under conditions of our experiment in contrast to R_fSF_3 (R = CF_3, i-C_2F_7) [28,42]. This may be due to intrinsic association and ready exchange in solution, or the presence of trace impurities (e.g. HF), which may facilitate exchange [43].

Vibrational Spectra

The infrared and Raman spectra of the new perfluoroalkyl derivatives are shown in Figures 1-4; and Tables 8-11, 14, 16-18, list the vibrational assignments for the individual compounds for the major bands made by comparison with the vibrational spectra of $(CF_3)_2Se_n$, (n = 1,2) [37], $(CF_3)_2S_n$ (n = 1,2) [44], SeF_4 [45-6], $(CH_3)_2SeF_2$ [20], $(CH_3)_2Se$ [47], $(CH_3)_2Se_2$ [48], $[(CF_3)_2CF]_2SF_2$ [49], SeF_3SbF_6 [50], SeF_5^- [51], $SeClF_5$ [52], and perfluoroethyl halides [53], the

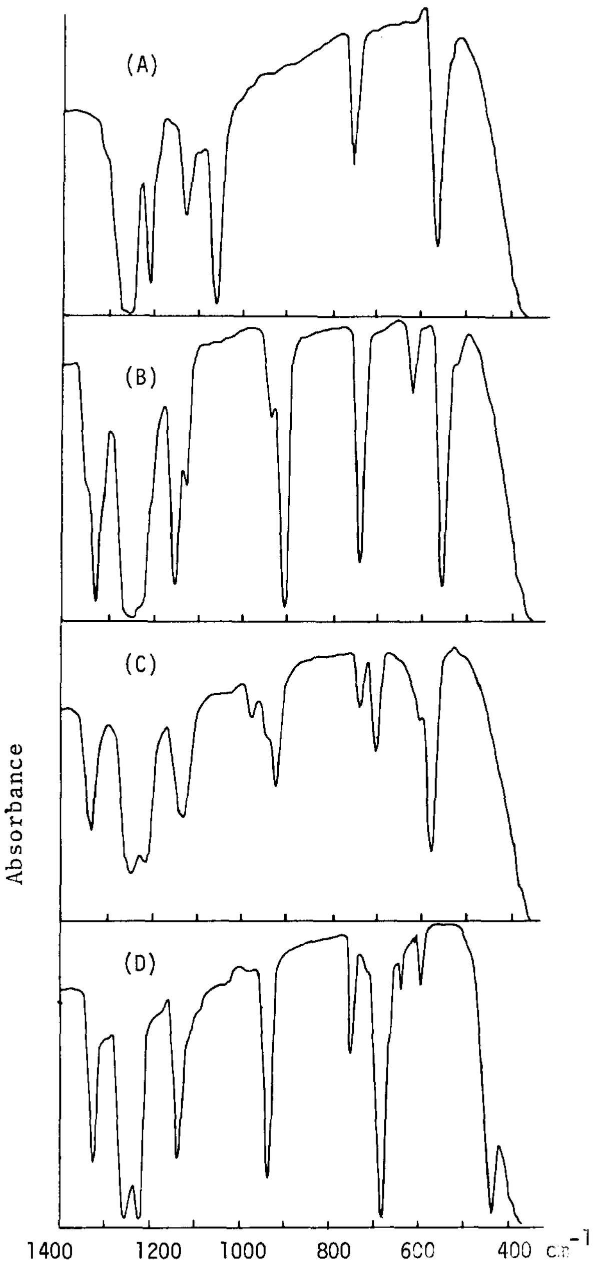


Figure 1. The infrared spectrum of gaseous; (A) $(CF_3)_2SeF_2$; (B) $(C_2F_5)_2SeF_2$; (C) $C_2F_5SeF_3$; (D) Trans $C_2F_5SeClF_4$.

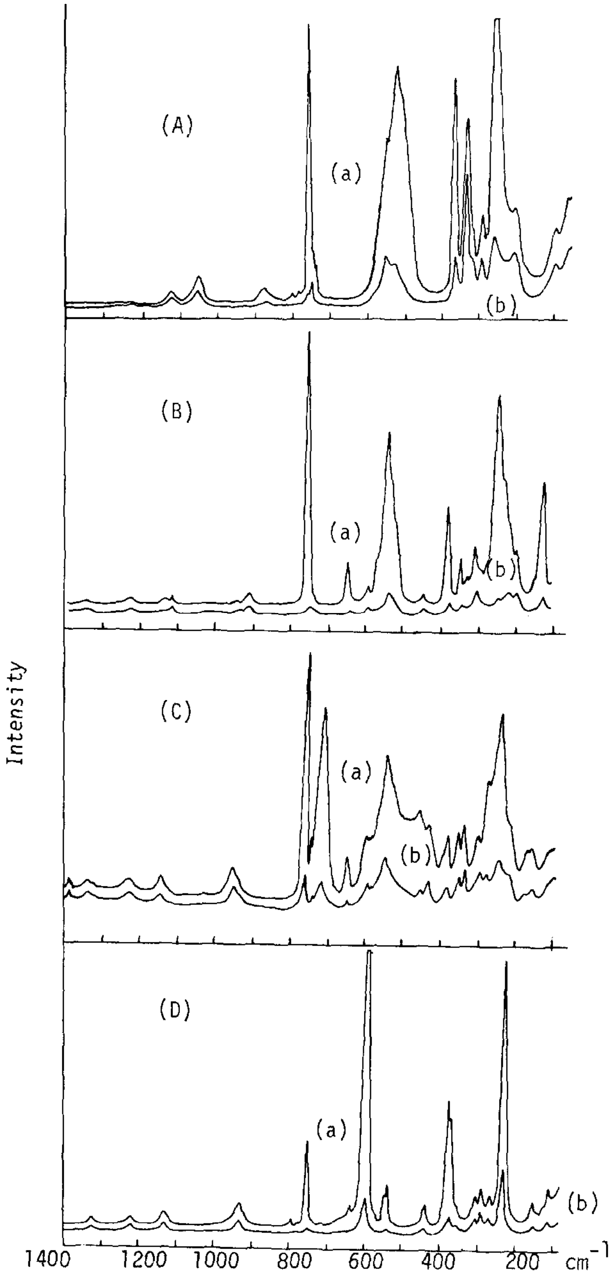


Figure 2. Raman spectrum of liquid; (A) $(CF_3)_2SeF_2$; (B) $(C_2F_5)_2SeF_2$; (C) C
(D) Trans $C_2F_5SeClF_4$. (a) Polarizer parallel (b) Polarizer perpend

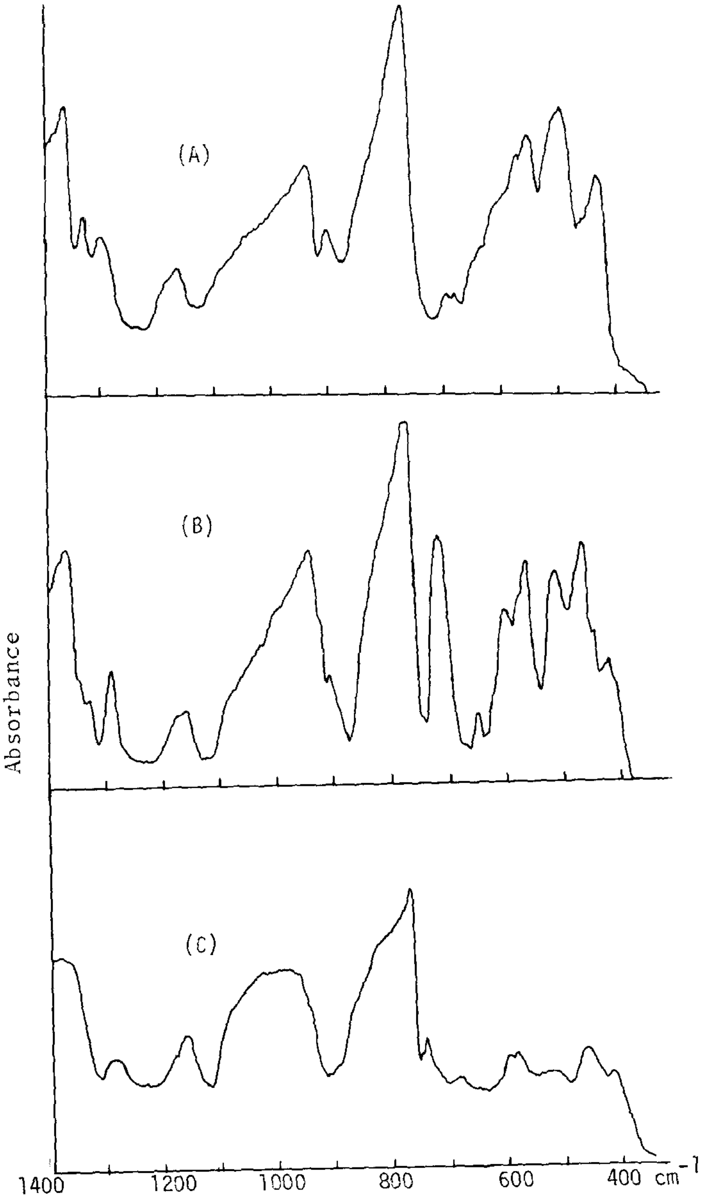


Figure 3. Infrared spectrum of solid; (A) $(C_2F_5)_2SeF_2.AsF_5$; (B) $(C_2F_5)_2SeF_2.$
(C) $C_2F_5SeF_3.SbF_5$.

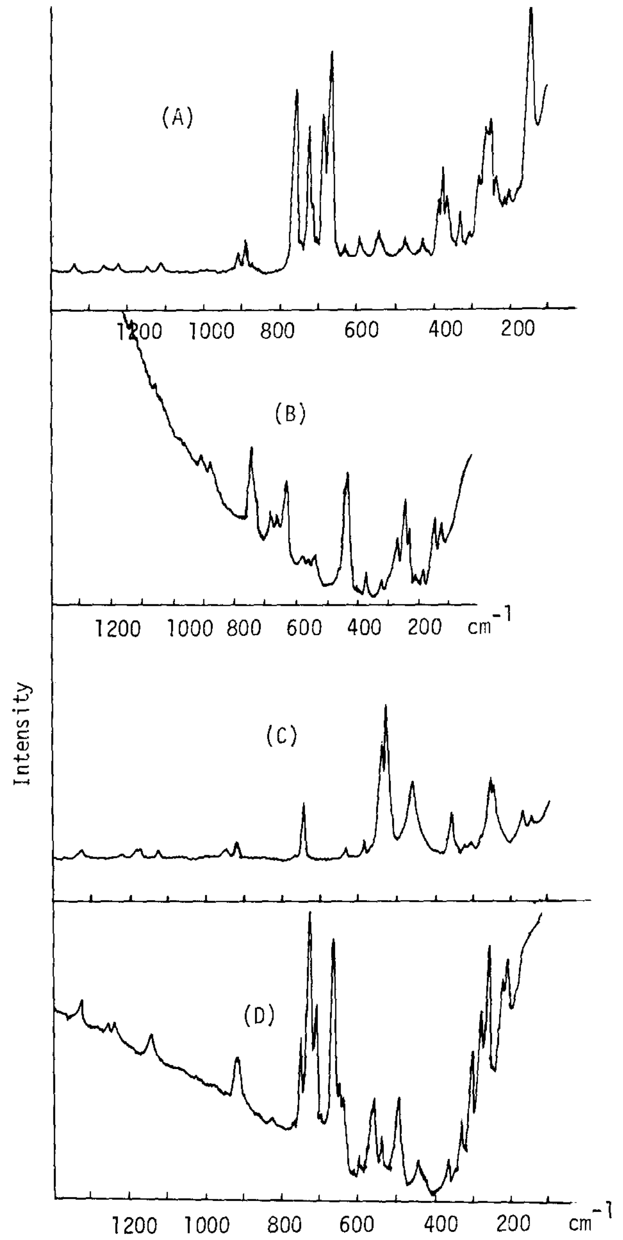


Figure 4. Raman spectra of solid; (A) $(C_2F_5)_2SeF_2.AsF_5$; (B) $(C_2F_5)_2SeF_2$ (C) $CsF.C_2F_5SeF_3$; (D) $C_2F_5SeF_3.SbF_5$.

Table 8. Vibrational spectrum of $(CF_3)_2SeF_2$

Infrared		Raman			
(cm^{-1})	I	(cm^{-1})	I	pol.	Tentative assignment
1310	w sh				C-F str. and combination modes
1285	m sh				
1265	vs				
1245	vs	1246	0.2	p	
1206	s	1200	<0.1	p	
1158	vw				
1125	m	1125	0.2	dp	
1090	vw				
1058	s	1051	0.6	p	
		888	0.3	p	
		802	<0.1	p	CF_3 deformation
		784	<0.1	p	
754	m	760	3.5	p	
		754(sh)		dp	
		740(sh)		p	
615	vw br	616	0.1	p	
		576(sh)		p	
568	s	558	0.7	dp	asym. $Se-F_{(ax.)}$ str.
535	w sh	533	10	p	sym. $Se-F_{(ax.)}$ str.
		519(sh)		p	CF_3 deformation
		370	2.3	p	C-Se sym. str. CF_3 rock
		335	1.5	dp	CF_3 rock
		324	0.4	dp	C-Se asym. str. CF_3 rock
		301	1.2	dp	F-Se-F asym. bend CF_3 rock
		261	7.1	p	CF_3 rock
		240(sh)		p(?)	CF_3 rock
		211	1.4	dp	F-Se-C deformation
		100	1.4	dp	C-Se-C bend
		43 (?)		dp	CF_3 torsion

s=strong, m=medium, w=weak, sh=shoulder, br=broad, v=very

Table 9. Vibrational spectrum of $(C_2F_5)_2SeF_2$

Infrared		Raman			
(cm^{-1})	I	(cm^{-1})	I	pol.	Tentative assignments
1348	w sh	1347	0.2	p	C-F str. and combination modes
1325	ms	1327	0.1	dp	
1258	s				
1228	m sh	1229	0.5	p	
		1214	0.4	p	
1155	ms	1154	0.4	p	
1138	w	1126	0.5	p	
945	w	944	0.4	p	C-C str.
910	s	908	1.1	p	
748	m	749	4.9	p	C_2F_5 deform.
632	w	647	0.8	p	
		598	0.7	dp	
568	s	568	1.0	p	asym. Se-$F_{(ax.)}$ str.
538	w sh	540	10	p	sym. Se-$F_{(ax.)}$ str.
		525	(sh)	p	C_2F_5 deform.
445	w br	442	0.4	dp	C_2F_5 rock
		374	2.3	p	C-Se sym. str. C_2F_5 rock
		346	0.8	p	C_2F_5 rock
		324	0.4	dp	C-Se asym. st. C_2F_5 rock
		304	1.5	dp	F-Se-F asym.bend
		249	7.4	p	C_2F_5 rock
		225	2.9	dp	C_2F_5 rock
		197	1.2	dp	F-Se-C bend
		159	0.3	p	C_2F_5 rock
		129	2.5	p	C-Se-C bend.C_2F_5 rock

vibrational spectra of bis(perfluoroethyl) sulphides $(C_2F_5)_2S_n$ (n = 1,2,3,4), selenides $(C_2F_5)_2Se_n$ (n = 1,2,3) tellurides $(C_2F_5)_2Te_n$ (n = 1,2) [54], and CF_3SF_5 [55].

In all of the spectra there are bands in the 1400-1100 cm^{-1} region which are readily assigned to C-F stretchings and combination modes of the CF_3 and C_2F_5 groups. In general,

Table 10. Vibrational spectrum of $C_2F_5SeF_3$*

Infrared		Raman			
(cm^{-1})	I	(cm^{-1})	I	pol.	Tentative assignment
		1380	0.6	dp	FEP tube
1339	ms	1330	0.4	p	C-F str.
		1296	0.4	dp	FEP tube
1255	s				C-F str.
1220	s	1220	0.6	p	
		1212	0.3	dp	FEP tube
1136	ms br	1140	0.4	p	C-F str.
985	w				imp?
950	m sh	941	0.6	p	C-C str.
932	m	926	0.2	dp	
752	w	751	3.5	p	C_2F_5 deform.
		729	1.0	p	FEP tube
718	m	707	5.8	p	Se-$F_{(eq.)}$ str.
638	w sh	635	0.6	p	C_2F_5 deform.
592	s	588	0.2	dp	asym.Se-$F_{(ax.)}$ str.
540	vw sh	541	10	p	sym. Se-$F_{(ax.)}$ str.
		480(vbr)			Se-F-Se bridging str.
450	w sh	445	2.2	p	C_2F_5 rock
		420	2.5	p	
		385	0.6	dp	FEP tube
		370	1.6	p	C-Se sym. st.
		343	1.0	dp	C-Se asym. st.
		326	1.0	dp	C_2F_5 rock
		299	1.4	p	sym. FSeF bend
		284	0.6	dp	FEP tube
		269	1.5	dp	C_2F_5 rock
		237	9.4	p	
		201(sh)		dp	F-Se-F deform, C_2F_5 rock
		159	1.3	p	C_2F_5 rock
		143	1.3	dp	C_2F_5 rock
		81	(?)	dp	C_2F_5 torsion

* spectrum was obtained in an FEP tube

Table 11. Vibrational spectrum of <u>trans</u> $C_2F_5SeClF_4$

Infrared		Raman			
(cm^{-1})	I	(cm^{-1})	I	pol.	Tentative assignment
1328	m	1330	0.2	p	C-F str. and combination modes
1258	s	1248	<0.1	dp	
1227	s	1228	0.2	p	
1136	m	1138	0.3	p	
980	vw	980	0.1	dp	C-C str.
940	s	939	0.4	p	
		802	0.1	p	C_2F_5 deform
		780	<0.1	p	
754	m	753	0.7	p	
720	w sh	720	<0.1	p	
689	s	682	0.3	dp	asym. SeF_4 str.
645	w	645	0.2	p	C_2F_5 deform.
598	w	596	10	p	sym. SeF_4 str.
		585	(sh)	dp(?)	ν_s SeF_4 out of phase
		552	0.2	p	C_2F_5 deform.
		546	0.5	p	
		448	0.1	dp	C_2F_5 rock
440	s	444	0.3	p	δs SeF_4
		378	1.3	p	$Se\text{-}Cl^{35}$ Str.
		371	0.4	p	$Se\text{-}Cl^{37}$ str.
		358	(sh)	dp	δs SeF_4 in plane
		308	0.4	dp	δas SeF_4 in plane
		293	0.5	dp	C_2F_5 rock
		273	0.4	dp	
		236	4.0	p	C-Se str. C_2F_5 rock
		157	0.4	p	$ClSeF_4$ Wagging
		115	0.5	p	C_2F_5 rock

no distinction is made between the CF_3 and CF_2 vibrations. In the 1000-850 cm^{-1} region, bands due to C-C vibrations of th C_2F_5 are present. There is a strongly polarized Raman band which has a counterpart in the infrared at about 750 cm^{-1}

which is assigned as a CF_3 or C_2F_5 deformations mode. Special attention will be focused on the Se-F stretching regions between 750 and 400 cm^{-1}, in which there are generally no intense bands attributable to other vibrations [37,54]. Many vibrations occur below 400 cm^{-1}, and assignments in this region are of a very tentative nature indeed.

(i) $(CF_3)_2SeF_2$.

The infrared and Raman spectrum of $(CF_3)_2SeF_2$ are shown in Figures 1 and 2 respectively and vibrational frequencies and tentative assignments are given in Table 8. In the region between 750-400 cm^{-1} there is a strong band at 568 cm^{-1} and a weak shoulder at about 535 cm^{-1} in the infrared which have counterparts in the Raman spectrum at 558 and 533 cm^{-1}. Since the 533 cm^{-1} Raman band in strong and polarized it is assigned as the symmetric F-Se-F stretching vibration, and the depolarized 558 band is assigned as the corresponding asymmetric stretching vibration. By comparison with the vibrational spectrum of monomeric SeF_4 [45], the 558 and 533 cm^{-1} vibrations are assigned to the axial asymmetric and symmetric vibrations respectively (See Table 12). The proposed structure of $(CF_3)_2SeF_2$ is therefore reasonably assigned trigonal bipyramid with a lone pair and perfluoromethyl groups in the equatorial plane and the two fluorine atoms occupying axial positions (I).

Wynne and coworkers [20] assigned the vibrational spectra of $(CH_3)_2SeF_2$ and reported axial asymmetric and symmetric stretching frequencies at 506 and 486 cm^{-1}. It would appear that the selenium fluorine stretching vibrations increase in frequency with increasing electronegativity of substituents.

(ii) $(C_2F_5)_2SeF_2$.

The infrared and Raman spectrum of $(C_2F_5)_2SeF_2$ are shown in Figures 1 and 2 and the tentative assignments in Table 9.

The infrared spectrum shows a strong band at 568 cm^{-1} and a weaker shoulder at 538 cm^{-1} which have counterparts in the Raman of a weak band at 568 cm^{-1} and a strong polarised band at 540 cm^{-1}. These bands are assigned to the axial asymmetric and symmetric F-Se-F stretching vibrations by analogy with $(CF_3)_2SeF_2$ and monomeric SeF_4 (Table 12). Since the asymmetric Se-F stretch at 568 cm^{-1} is polarised, it implies that perhaps the symmetry of $(C_2F_5)_2SeF_2$ (I) may be less than C_{2v}.

(iii) $C_2F_5SeF_3$.

The infrared and Raman spectra are shown in Figures 1 and and tentative assignments for $C_2F_5SeF_3$ are given in Table 10.

The infrared spectra shows a band at 718 cm^{-1} with a corresponding band at 707 cm^{-1} in the Raman, which is assigned to the equatorial Se-F stretching vibration by comparison with the vibrational spectrum of SeF_4 [45] (See Table 12). By analogy to $(CF_3)_2SeF_2$ and $(C_2F_5)_2SeF_2$, the strong band at 592 cm^{-1} and weak shoulder at 540 cm^{-1} in the infrared spectrum with counterparts in the Raman at 588 and 541 cm^{-1} (strongly polarised) are reasonably assigned to the axial asymmetric and symmetric stretching vibrations respectively. The geometry of $C_2F_5SeF_3$ is therefore reasonably established as being based on a trigonal bipyramid with a lone pair and C_2F_5 group in the equatorial plane, and the other positions being occupied by fluorines (II). There is also a broad band between 600-400 cm^{-1} in the Raman spectrum, which has been observed in liquid SeF_4 [46], and reported to arise from molecular association. It would appear that the compound is monomeric in the gas phase at lower pressures but is associated in the liquid phase.

Table 12. Comparison of Se-F stretching frequencies (cm^{-1}) in SeF_4 and its derivatives

Compound	sym. Se-$F_{(eq)}$	asym. Se-$F_{(eq)}$	sym. Se-$F_{(ax)}$	asym.S
SeF_4 [a]	747	733	571	62
$C_2F_5SeF_3$	707		541	58
$(C_2F_5)_2SeF_2$	___		540	56
$(CF_3)_2SeF_2$	___		533	55
$(CH_3)_2SeF_2$ [b]	___		486	50

[a] Reference 45. [b] Reference 20.

(iv) Trans $C_2F_5SeClF_4$.

The ^{19}F n.m.r. study of trans $C_2F_5SeClF_4$ confirmed the trans configuration of the molecule. If the C_2F_5 group can be considered as freely rotating then trans $C_2F_5SeClF_4$ has pseudo C_{4v} symmetry (III). The vibrational assignment of trans $C_2F_5SeClF_4$ should show similar Se-F and Se-Cl bands to those observed for $SeClF_5$ with the exception of those involving the axial fluorine.

The infrared and Raman spectra of trans $C_2F_5SeClF_4$ and the vibrational assignments are shown in Figures 1,2, and Table 11 respectively. The strong polarised band in the Raman at 596 cm^{-1} with a weak counterpart in the infrared at 598 cm^{-1} is readily assigned to the symmetric $SeF_{4(eq.)}$ stretching vibration. The polarised peak in the Raman at 444 cm^{-1} with a strong counterpart in the infrared at 440 cm^{-1} is assigned as the symmetric $SeF_{4(eq.)}$ out of plane bending vibration, and the strongly polarised bands at 378 and 371 cm^{-1} are assigned to $Se-Cl^{35}$ and $Se-Cl^{37}$ stretching vibrations respectively. The isotopic splittings and relative intensities are in good agreement with these assignments. The strong peak in the infrared at 689 cm^{-1} with a weak counterpart in the Raman at 682 cm^{-1} is assigned as the asymmetric $SeF_{4(eq.)}$ vibration. The assignments for the other modes are of a very tentative nature. The corresponding $Se-F_{4(eq.)}$ and Se-Cl stretching frequencies decrease from $SeClF_5$ [52] to trans $C_2F_5SeClF_4$ as expected, and are compared in Table 13.

(v) $CsF.C_2F_5SeF_3$.

The Raman spectrum of $CsF.C_2F_5SeF_3$ is given in Fig. 4, and the list of frequencies and assignments in Table 14. The infrared spectrum was obtained with both AgCl and KBr plates but were of poor quality therefore not included. The Raman spectrum is very similar to that observed for $Cs^+SeF_5^-$ [51], and in addition there are bands attributable to the C_2F_5 group present. The vibrational spectrum of $Cs^+SeF_5^-$ was assigned based on C_{4v} symmetry of the SeF_5^- ion.

Table 13. Comparison of Se-F and Se-Cl stretching frequencies of $SeClF_5$ and $C_2F_5SeClF_4$

Assignment in point group C_{4v}	$SeClF_5$[a] i.r.[b]		Raman	$C_2F_5SeClF_4$ i.r.	Raman
a_1 ν_1 $\nu(SeF')$	729	ms sh	721 (1.8)p	—	—
ν_2 $\nu_s(SeF_4)$	654	w	656 (10)p	598 w	596 (10)p
ν_3 $\delta_s(SeF_4)$ out of plane	440	vs	443 (2.2)p	440 s	444 (0.4)p
ν_4 $\nu(SeCl^{35})$	394	mw	385 (8.5)p	—	378 (1.3)p
$\nu(SeCl^{37})$			380		371 (0.4)p
b_1 ν_5 $\nu_s(SeF_4)$ out of phase	—		636 (0.6)dp	—	585 (0.5)
ν_6 $\delta_{as}(SeF_4)$ out of plane	—		—	—	—
b_2 ν_7 $\delta_s(SeF_4)$ in plane	—		380 dp	—	358 (0.3) dp ?
e ν_8 $\nu_{as}(SeF_4)$	745	vvs	745 (0.3)dp	689 s	682 (0.3)dp
ν_9 $\delta(F'SeF_4)$	421	s	424 (0.4)dp	—	—
ν_{10} $\delta_{as}(SeF_4)$ in plane	334	m	336 (1.2) dp	—	308 (0.4)dp ?
ν_{11} $\delta(ClSeF_4)$	—		213 (1.4)dp	—	157 (0.4)p ?

[a] Reference 52

[b] All frequencies given in cm^{-1}

Table 14. Vibrational spectrum of $CsF.C_2F_5SeF_3$

Infrared (cm^{-1})	I	Raman (cm^{-1})	I	Tentative assignment
1322	s	1320	0.8	C-F str. and combination modes
1225	s			
1170	s	1170	1.0	
1118	s	1120	0.5	
942	s	946	1.0	C-C str.
898	m	902	1.5	
748	m	745	2.2	C_2F_5 deform.
640	w	636	0.3	
588	w	588	0.4	
		544	3.4	C_2F_5 rock, $\nu_s(SeF_4)$?
530	m	530	10	ν_s (SeF_4) in plane
		485(sh)		$\nu_{as}(SeF_4)$?
460	s br	461	7.2	$\nu_s(SeF_4)$ out of phase, $\nu_{as}(SeF_4$
		440(sh)		C_2F_5 rock, ν_{as} (SeF_4)?
360	m	358	2.2	δ_s (SeF_4) umbrella
		325	0.6	C_2F_5 rock, C-Se
		310	0.7	δ_s (SeF_4) in plane
		281(sh)		C_2F_5 rock
		258	9.0	
		234(sh)		
		169	2.9	δ_{as} (SeF_4)
		143	2.3	C_2F_5 rock

$CsF.C_2F_5SeF_3$ shows similar bands with the absence of vibrational modes involving axial Se-F' and F'$SeF_{4(eq.)}$ wagging. The bands involving the SeF_4 part of the spectrum are compared with SeF_5^- in Table 14. The band at 544 cm^{-1} in Raman may be due to C_2F_5 or it may involve an $SeF_{4(eq.)}$ stretching mode caused by the reduction of symmetry for $C_2F_5SeF_4^-$ from the idealized C_{4v}, or, perhaps due to solid state effects. However, the strong band at 530 cm^{-1} in the Raman is clearly due to the $SeF_{4(eq.)}$ symmetric stretch. There is a strong band in the infrared at 460 cm^{-1} which

Table 15. Comparison of Se-F stretching frequencies of $Cs^+SeF_5^-$ [a] and $CsF.C_2F_5SeF_3$

Assignment in point group C_{4v}	$Cs^+SeF_5^-$ i.r.[b]		Raman		$CsF.C_2F_5SeF_3$ i.r.		Raman	
A_1 ν_1 $\nu(SeF')$	665	vs	666	(10)	—		—	
ν_2 ν_s (SeF_4) in plane	520	sh	515	(7.5)	530	m	530	(10)
ν_3 δ_s (SeF_4) umbrella	335	s	332	(3.2)	360		358	(2.2)
B_1 ν_4 ν_s (SeF_4) out of phase	—		460	(7.0)	—		[461	(7.2)]
ν_5 δ_{as} (SeF_4) out of plane	—		236	(0.6)	—		—	
B_2 ν_6 δ_s (SeF_4) in plane	—		282	(2.6)	—		310	(0.7)
E ν_7 ν_{as} (SeF_4)	475	vs br	480	(sh)	460	s br	[461	(7.2)]
ν_8 δ $(F'SeF_4)$	398	mw	399	(1.9)	—		—	
ν_9 δ_{as} (SeF_4) in plane	—		202	(0.7)	—		169	

[a] Reference 51

[b] All frequencies given in (cm^{-1})

Table 16. Vibrational Spectrum of $C_2F_5SeF_3.SbF_5$

Infrared		Raman		
(cm^{-1})	I	(cm^{-1})	I	Tentative assignment
1319	m	1320	1.3	C-F str. and combination modes
1255	s br	1256	0.8	
1225	s br	1229	1.7	
1138	m sh	1136	1.2	
1122	s			
950	w sh			C-C str.
918	s	916	3.8	
758	m	752	2.8	C_2F_5 deform.
740	m	732	10	$C_2F_5SeF_2^+$ (Se-F) str.
708	s br	714	5.9	$C_2F_5SeF_2^+$ (Se-F) str.
		690	0.1	SbF_6^- ν_1^* and ν_3
660	s v br	666	8.2	
		652 (sh)		
638	s br	640 (sh)		
590	w	595	0.9	SbF_6^- ν_2
555	m	560	5.4	
		538	2.5	
490	m	495	6.7	SbF_6^-, $Sb_2F_{11}^-$ imp?
425	m	442	2.9	C_2F_5 rock, C-Se, SbF_6^- ν_4
		368	1.4	
		328	1.6	
		303	4.7	SbF_6^- ν_5
		281	5.0	
		271	0.1	
		261	6.0	C_2F_5 rock
		225	3.8	
		216	3.4	

* based on octahedral symmetry

has a counterpart at 461 cm^{-1} in the Raman which may be the asymmetric $SeF_{4(eq.)}$ stretch and/or it may be the symmetric out of phase stretch corresponding to ν_4 of SeF_5^-, and either shoulders at 485 and 440 cm^{-1} may be due to the

Table 17. Vibrational spectrum of $(C_2F_5)_2SeF_2.SbF_5$

Infrared		Raman		
(cm^{-1})	I	(cm^{-1})	I	Tentative assignment
1338	m			C-F str. and combination modes
1312	s			
1230	s br			
1205	s br			
1125	s br	1127	0.8	
1105	s br			
912	w	911	1.3	C-C str.
875	s	880	1.9	
753	m sh	751	4.8	C_2F_5 deform.
733	s	730 (sh)		$C_2F_5SeF^+$ (Se-F) str.
		694	2.6	SbF_6^- ν_1, ν_3.
660	s	665	2.9	
638	s	637	4.7	
582	w	582	1.7	SbF_6^- ν_2
567	w sh	562	0.5	
532	m	536	3.7	
485	w			SbF_6^- ?
442	w sh	437	10	C_2F_5 rock ?
430	m			
		372	1.0	SbF_6^- ν_4?
		320	0.8	$C_2F_5SeF^+$ deform? C-Se?
		277	4.2	SbF_6^- ν_5
		250	5.8	C_2F_5 rock, C-Se etc.
		236	2.3	
		211	0.8	
		189	1.3	
		153	4.4	
		132	1.7	

asymmetric $SeF_{4(eq.)}$ stretch. Despite these ambiguities the Raman spectrum is sufficiently like that of SeF_5^-, (See Table 15) to show that the adduct very probably has the ionic structure, $Cs^+C_2F_5SeF_4^-$ (IV).

Table 18. Vibrational spectrum of $(C_2F_5)_2SeF_2.AsF_5$

Infrared		Raman		
(cm^{-1})	I	(cm^{-1})	I	Tentative assignment
1349	w	1349	0.3	C-F str. and combination modes
1318	w	1301	0.1	
1260	s sh	1259	0.1	
1228	vs br	1232	0.1	
1148	m	1148	0.2	
1125	s br	1122	0.2	
922	w	923	1.5	C-C str.
885	m	894	1.9	
		882	0.2	
755	m sh	755	4.1	C_2F_5 deform.
725	s br	731	2.5	$C_2F_5SeF^+$ (Se-F) str.
		723(sh)		AsF_6^- ν_1, ν_3
690	ms	689	3.6	
670	s	675	6.2	
646	m sh	644	0.3	
590	vw	593	0.9	AsF_6^- ν_2
532	w	542	1.0	
465	m br	477	0.3	?
		442	0.3	C_2F_5 rock
		384	0.7	AsF_6^- ν_4
		375	2.5	AsF_6^- ν_5
		357	1.0	
		332	1.1	C_2F_5 rock, C-Se, etc.
		287	0.9	
		261	1.9	
		256	2.0	
		241	0.5	
		207	0.6	
		133	10	

(vi) $(C_2F_5)_2SeF_2.AsF_5$, $(C_2F_5)_2SeF_2.SbF_5$ and $C_2F_5SeF_3.SbF_5$.

The infrared and Raman spectra of $C_2F_5SeF_3.SbF_5$, $(C_2F_5)_2SeF_2.SbF_5$ and $(C_2F_5)_2SeF_2.AsF_5$ are shown in Figures 3 and 4 respectively, and tentative assignments of vibration spectra of these complexes are listed in Tables 16-18. All spectra show bands due to AsF_6^- and SbF_6^- [56,57] however, there are more bands than that expected for full octahedral symmetry. Similar effects have been observed with complexes of selenium tetrafluoride with Lewis acids and attributed by Gillespie and Whitla [50] to cation-anion bridging. This has been confirmed by the crystal structures of $SeF_4.NbF_5$, $SeF_4.TaF_5$, and $SeF_4.2NbF_5$ [58,59] which show that these adduc are predominately ionic with significant interaction through fluorine bridging. The Raman bands at 731 cm^{-1} in $(C_2F_5)_2SeF_2.AsF_5$, 730 cm^{-1} in $(C_2F_5)_2SeF_2.SbF_5$ as well as 732 and 714 cm^{-1} in $C_2F_5SeF_3.SbF_5$ may be attributed to Se-F stretching of the $(C_2F_5)_2SeF^+$ and $C_2F_5SeF_2^+$ ions (V) and (VI) by comparison with various SeF_3^+ containing salts (Table 19). The Se-F stretching frequencies of the perfluoroethyl adducts are less than those of SeF_3^+ as expected in replacement of the fluorine by the less electronegative C_2F_5 group. A similar situation is found for SF_3^+ [60,61] relative to the

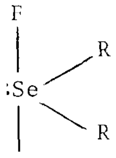
Table 19. Comparison of Se-F stretching frequencies of some Se-F containing cationic complexes.

Compound	Se-F (cm^{-1})		Reference
	sym. st.	asym. st.	
$SeF_3^+SbF_6^-$	775	742	50
$SeF_3^+AsF_6^-$	774	754	50
$SeF_3^+NbF_6^-$	769	724	50
$SeF_3^+TaF_6^-$	773	740	50
$SeF_3^+BF_4^-$	763	730	50
$(C_2F_5)_2SeF^+SbF_6^-$	730		this work
$(C_2F_5)_2SeF^+AsF_6^-$	731		this work
$C_2F_5SeF_2^+SbF_6^-$	732	714	this work

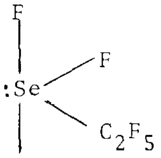
corresponding $CF_3SF_2^+$ salts [62]. The spectra are consistent with the adducts being mainly ionic with substantial anion-cation interaction through fluorine bridging.

Structural Conclusions

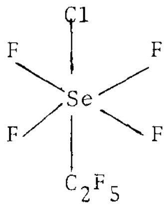
The structures of $(CF_3)_2SeF_2$ and $(C_2F_5)_2SeF_2$ have been established (I), as monomeric in the gaseous and liquid phases, whereas $(C_2F_5)_2SeF_3$ (II) is associated in the liquid phase. $C_2F_5SeClF_4$ is monomeric and has the trans configuration (III). The salt $Cs^+C_2F_5SeF_4^-$ (IV) appears to be an ionic salt, whereas $(C_2F_5)_2SeF^+$ (V) and $(C_2F_5)_2SeF_2^+$ (VI) are essentially ionic but also are fluorine bridged to the corresponding counter ions.



(I) R = CF_3, C_2F_5



(II)



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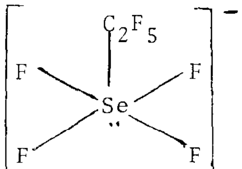

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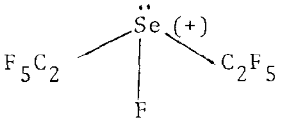

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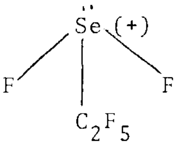

(VI)

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