ADVANCES IN INORGANIC CHEMISTRY AND RADIOCHEMISTRY, VOL. 24

SELENIUM AND TELLURIUM FLUORIDES

A. ENGELBRECHT and F. SLADKY

Institut für Anorganische und Analytische Chemie, Universität Innsbruck, Innsbruck, Austria

I. Introduction

This review is conceived as a progress report. It includes only compounds of selenium and tellurium with the element directly bonded to fluorine. The chemical literature of the last 10 years, including 1979, has been searched thoroughly, and emphasis has been placed on facts rather than on interpretation. There are some earlier reviews covering the same area: "Fluorine Compounds of Selenium and Tellurium" 1970 (*40*), "Inorganic Selenium Chemistry" 1975 (*48*), and "Inorganic Chemistry of Tellurium" 1975 (*63*).

ISBN 0-12-023624-9

II. Fluorides of Lower Oxidation States

A. THE SeF RADICAL

Gas-phase electron resonance spectra of SF and SeF have been evaluated for the corresponding bond lengths (*31*). The values for S—F (1.599 ± 0.002 Å) and Se—F (1.742 ± 0.005 Å) are very close to the bond lengths reported for the molecules SF_2 (1.59 Å) and SeF_2 (1.69 Å) deduced from infrared spectra (*88*).

B. Se_2F_2 AND SeF_2

The reaction of selenium heated to 210°C and fluorine, highly diluted with argon, leads to a mixture of lower fluorides of selenium (*88*). Investigation of the infrared spectra of the products trapped at low temperature allowed the unambiguous identification of SeF_2 and FSe—SeF. Ultraviolet photolysis of FSe—SeF converts it partially into $Se{=}SeF_2$. Table I summarizes the derived valence force constants and geometries of these compounds in comparison to related molecules (*88*). Bond properties in the series OF_2, SF_2, SeF_2 show a trend similar to the trend in the series O_3, SO_2, SeO_2 (Table II). SF_2 and SeF_2, judged by their force constants, should be stable species although they obviously are too reactive to have been synthesized in preparative amounts.

III. Tetrafluorides

As is apparent from the melting and boiling points of the tetrafluorides, SeF_4 and TeF_4 are strongly associated in the condensed phase. Evalution of the specific molecular parameters of the discrete

TABLE I

VALENCE FORCE CONSTANTS[a] AND GEOMETRIES OF BINARY SELENIUM FLUORIDES

Compound	f_R	f_r	Ref.	R	r	β	α	Ref.
$Se{=}Se$	3.49		*14*	2.16				*14*
FSe—SeF		3.25	*88*	2.25	1.77	100	90	*88*
$Se{=}SeF_2$	3.67	3.07	*88*	2.15	1.77	100	90	*88*
SeF_2		4.29	*88*		1.69		94	*88*
SeF_4		3.38/5.04	*23*		1.77/1.68			*2*
SeF_6		4.95	*66*		1.69			*24*

[a] $\times 10^2$ N m^{-1}. R = Se—Se bonding; r = Se—F bonding (Å); β = $\widehat{FSeF}$ angle; α = dihedral $\widehat{FSeF}$ angle.

TABLE II

FORCE CONSTANTS[a] AND GEOMETRIES OF SOME CHALCOGEN FLUORIDES AND OXIDES

Compound	f_r	f_{rr}	Ref.	r	α	Ref.
OF_2	3.95	0.81	*167*	1.409	103.3	*167*
SF_2	4.72	0.37	*87*	1.59	98.2	*100*
SeF_2	4.29	0.24	*167*	1.69	94	*31*
O_3	5.70	1.52	*167*	1.276	117	*167*
SO_2	10.02	0.03	*167*	1.432	119	*167*
SeO_2	6.9	0.03	*185*	1.607	113.5	*185*

[a] $\times 10^2$ N m^{-1}.

molecules therefore required special techniques, high accuracy in measurements, and careful interpretation of the results. Microwave, infrared, and Raman spectroscopy were applied, including matrix isolation studies. Some of the results are summarized in Table III and compared to SF_4. All discrete molecules have C_{2v} symmetry. The differences in lengths of axial and equatorial M—F bonds are remarkably similar.

A. SeF_4

SeF_4 has been prepared in various reactions involving a fluorinating agent (AgF, ClF, ClF_3, CoF_3, SF_4, F_2, BrF_3) acting upon elemental selenium, SeO_2, $SeCl_2$, or $SeCl_4$. A rather convenient method of prepara-

TABLE III

PHYSICAL PROPERTIES AND MOLECULAR PARAMETERS OF GROUP VI TETRAFLUORIDES[a]

Property	SF_4	SeF_4[b]	TeF_4[c]
mp (°C)	−121 (*133*)	−9.5 (*133*) −38.87 (*147*) −39 ± 9 (*29*)	129 (*28*)
bp (°C)	−38	101.0	374 (*133*)
R_{ax} (Å)	1.646 (*188*)	1.771 (*23*)	1.90 (*2*)
R_{eq} (Å)	1.545 (*188*)	1.682 (*23*)	1.79 (*2*)
F_{eq}—M—F_{eq}	101.43 (*188*)	100.55 (*23*)	
F_{ax}—M—F_{ax}	172.73 (*188*)	169.20 (*23*)	

[a] References are given in parentheses.

[b] See also Table IV.

[c] See also Table VIII.

TABLE IV

PHYSICAL PROPERTIES OF SeF_4[a]

Property		Ref.
Heat of vaporization (cal mol^{-1})	11,240	*133*
Entropy of vaporization (eu)	30.0	*133*
Heat of fusion (cal mol^{-1})	557	*147*
	290±140	*29*
Standard heat of formation, $\Delta H_f^\circ(298^\circ)$ (kcal mol^{-1})	-203.0 ± 5.8	*30*
Liquid density, 25°C (g ml^{-1})	2.72	*133*
Dipole moment (D)	1.779	*23*

[a] See also Table III.

tion was reported recently (*129*), using SeF_4 itself as the reaction medium according to Eq. (1):

$$3Se + 4ClF_3 \xrightarrow[90^\circ C]{SeF_4} 3SeF_4 + 2Cl_2 \quad (1)$$

Some of its most important physical properties have recently been reinvestigated. A large discrepancy exists between the values reported for the melting point of SeF_4. While an earlier value is given as −9.5°C (*133*), vitreous fusion between −48 and −30°C was reported in 1979 (*29*), i.e., −39 ±9°C as a median value, surprisingly close to the melting point of −38.87°C listed in (*147*). Table IV summarizes some physical properties of SeF_4.

SeF_4 has been suggested as a fluorinating agent in organic chemistry as it has some advantage over SF_4 in the fluorination of ketones, aldehydes, amides, alcohols, carboxylic acids, and anhydrides. The use of SeF_4 permits milder conditions, and because of its convenient liquid range, it can be employed at atmospheric pressure (*129*).

SeF_4, which has been reported to react with ClF at 350°C to yield a mixture of SeF_5Cl, Cl_2, and SeF_6 in about equal amounts, does not

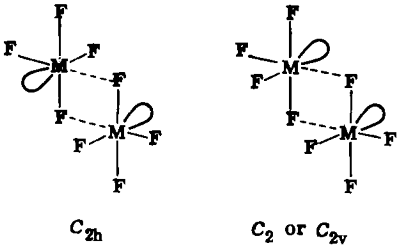


FIG. 1. Suggested structures of SeF_4 and TeF_4 dimers. From Adams and Downs (*2*).

TABLE V

ASSIGNMENT OF FUNDAMENTALS FOR SF_4, SeF_4, AND TeF_4

Class	Assignment	SF_4[a]	SeF_4[b]	TeF_4[c]	Approximate description
a_1	ν_1	891.5	747	695.0	Sym. str., eq. MF_2
	ν_2	558.4	571	572	Sym. str., ax. MF_2
	ν_3	464.5	409	333.2	Scissors, eq. MF_2
	ν_4	226	156	(151.5)[d]	Scissors, ax. MF_2
a_2	ν_5	414(?)	—	—	Torsion
b_1	ν_6	730	622	586.9	Asym. str., ax. MF_2
	ν_7	532.2	361	273.3	Rocking
b_2	ν_8	867.0	733	682.2	Asym. str., eq. MF_2
	ν_9	353	250	(184.8)[d]	Waging

[a] Vapor phase (*35, 77, 116*).

[b] Vapor phase (*2*).

[c] N_2 matrix (*2*).

[d] Calculated (*2*).

react with either HCl or HF under the same conditions (*41*). Earlier attempts to synthesize SeF_5Cl from SeF_4 (via Se + ClF) and ClF in a Monel cylinder at the somewhat lower temperature of 200°C failed (*134*).

Detailed investigations of the vibrational spectra, including matrix isolation studies (*2*), essentially confirm the results of microwave spectroscopy (*23*). The high quality of the spectra in very dilute matrices even showed individual peaks due to the five naturally occurring selemium isotopes (*2*). More concentrated matrices contain absorptions arising from several dimeric or oligomeric species. The intensity of such absorptions was also seen to grow on diffusion of more dilute matrices. Two possible structures for the dimers $(SeF_4)_2$, differing in the mutual orientation of the equatorial groupings, are suggested (Fig. 1).

Tentative assignments of fundamental frequencies observed for the discrete SeF_4 and TeF_4 molecules compared to the assignments for SF_4 are listed in Table V (*2*). High-temperature Raman studies of SeF_4 (*5*) confirm considerable interactions of the molecules in the liquid and solid state. Solid SeF_4 apparently exists in two forms (*5*).

1. SeF_4 in Solution

Conductometric measurements of SeF_4 in liquid hydrogen fluoride prove it to be a weak base (*25*) [Eq. (2)]:

$$SeF_4 + HF \rightarrow SeF_3^+ + HF_2^- \qquad (2)$$

TABLE VI

^{19}F-NMR DATA FOR SeF$_4$[a]

δ_F	δ_A	δ_B	J_{AB}	$J_{^{77}Se-A}$	$J_{^{77}Se-B}$	Ref.
−28.7[b]	−37.7	−12.1	26	302	1200	*161*

[a] The chemical shifts are with reference to CFCl$_3$ at −140°C.
[b] At 20°C.

The estimated value of the ionization constant $K_b = 4 \times 10^{-4}$ indicates that SeF$_4$ is a weaker base in HF than SF$_4$ ($K_b = 4 \pm 2 \times 10^{-2}$) (*11*).

SeF$_4$ is reported to be rather soluble in CH$_3$F (~10% at −140°C, ~40% at −125°C), recommending such solutions for ^{19}F-NMR investigations. The temperature dependence of the spectrum confirms the presence of an A$_2$B$_2$ spin system and fast intramolecular exchange at room temperature (*161*), according to a BERRY-type mechanism (*146*). The coalescence temperature is about −80°C, with an estimated energy barrier of 6–9 kcal mol^{-1} (*146*). The intensity of the coupling of ^{19}F to ^{77}Se (natural abundance 7.5%, spin ½) is a further confirmation that discrete molecules are present, even at −140°C. Table VI lists the ^{19}F-NMR data at varying temperatures.

The vapor pressure of solutions of SeF$_4$ in CH$_3$F allowed a rough estimation of the molecular weight of the dissolved species, which again confirms that no measurable association (via Se—Se) takes place. A Raman investigation of these solutions at −130°C allows an interpretation in terms of distinct SeF$_4$ molecules with only slight indications of F—F bridges in concentrated solutions (*161*).

2. *SeF$_4$ and Lewis Acids*

The question as to the best formulation of structures and species in some binary fluoride systems was the subject of extensive experimental investigations, involving infrared and Raman spectroscopy in the molten state and in solutions as well as NMR spectroscopy and conductometric and cryoscopic measurements. Some crystal structure studies have also been published. The systems of SeF$_4$ with BF$_3$, SbF$_5$, AsF$_5$, NbF$_5$, and TaF$_5$ have been studied recently.

Raman spectra of the complexes of SeF$_4$ with AsF$_5$ and SbF$_5$ in the molten state have been interpreted as confirming the ionic-type formulation (SeF$_3$)$^+$(SbF$_6$)$^-$, analogous to (SF$_3$)$^+$(SbF$_6$)$^-$ (*65*).

Investigation of NMR spectra, vibrational spectroscopy, and the analysis of conductometric behavior of the adducts of SeF$_4$ with AsF$_5$,

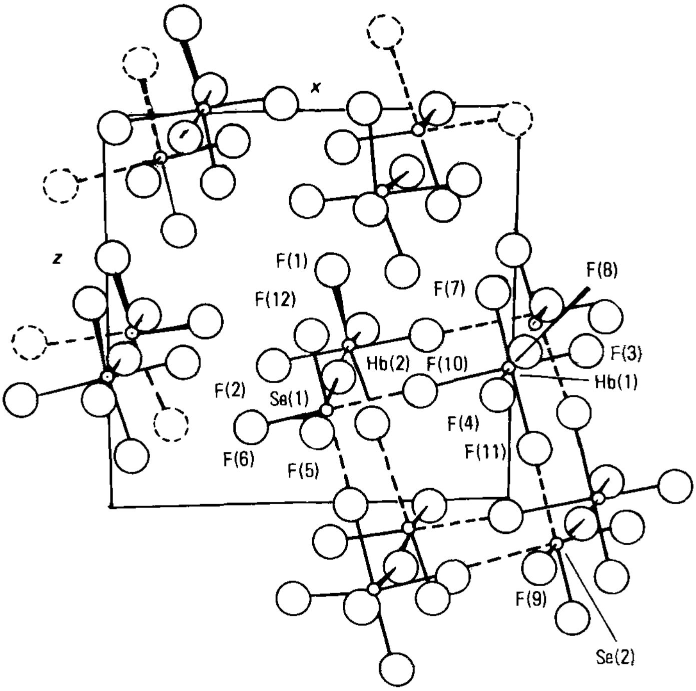


FIG. 2. Atomic arrangement in $SeF_4 \cdot NbF_5$, showing the projection down (010). From Edwards and Jones (*53*).

SbF_5, BF_3, NbF_5, and TaF_5 led likewise to the conclusion that, in the solid state, these compounds are best formulated as predominantly ionic, although the ions interact rather strongly by fluorine bridging. This bridging apparently persists in the molten state and to some extent in solution in nitrobenzene (*25, 82*).

Solutions of $SeF_4 \cdot BF_3$ in HF are considered to contain an equilibrium mixture as shown in Eq. (3), involving a dimer $(SeF_4 \cdot BF_3)_2$ with some additional fluorine exchange mechanism involving SeF_3 and BF_3.

$$(SeF_4 \cdot BF_3)_2 \rightarrow (SeF_3)_2 \cdot BF_4^- + BF_4^- \qquad (3)$$

SeF_4 interacts with NbF_5, depending on the temperature, to form the adducts $SeF_4 \cdot 2NbF_5$ (room temperature) or $SeF_4 \cdot NbF_5$ (at 106°C) (*52, 53*); with TaF_5, the adduct $SeF_4 \cdot TaF_5$ is formed.

A crystal structure analysis proved $SeF_4 \cdot NbF_5$ to have the same unit-cell dimensions as $SeF_4 \cdot TaF_5$. The atomic arrangement in the rhombohedral crystals is shown in Fig. 2 and is consistent with the ionic formulation $(SeF_3)^+(NbF_6)^-$, with, however, substantial fluorine

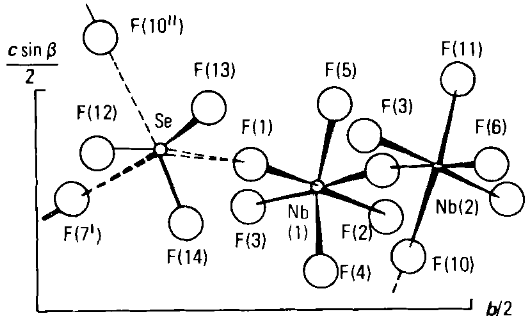


Fig. 3. Atomic arrangement in $SeF_4 \cdot 2NbF_5$, showing the projection down (100). From Edwards and Jones (*53*).

bridging between the ions to form tetrameric units. The adduct $SeF_4 \cdot 2NbF_5$ is also best formulated ionically as $(SeF_3)^+(Nb_2F_{11})^-$ with substantial fluorine bridging of the ions (Fig. 3). Average bond distances are tabulated in Table VII, together with data for SeF_4 (*23*) and SbF_5 (*50*).

SeF_4 also forms an adduct with SO_3 which has been investigated in the solid state, the molten state, and in solution (*81*). The results of infrared, Raman, and NMR studies and some conductometric and cryoscopic measurements can best be interpreted consistently in terms of a polymeric fluorosulfate bridged structure for the solid and the molten compound. There is also evidence for either a cyclic or linear dimer in dilute solutions in nitrobenzene or HSO_3F (Fig. 4).

Formation of a new compound $PSeF_3$ has been claimed in the reaction of PF_3 with elemental selenium, at 300–400°C, identified from a mass spectrum analysis, showing the fragments $(PSeF_2)^+$ with the expected selenium isotopes (*34*). However, since no further data have been obtained, it appears very likely that the compound actually was

TABLE VII

Average Bond Distances (Å) in $SeF_4 \cdot NbF_5$, $SeF_4 \cdot 2NbF_5$, SeF_4, and NbF_5

Compound	$(SeF_3)^+(NbF_6)^-$ (*53*)	$(SeF_3)^+(Nb_2F_{11})^-$ (*53*)	SeF_4 (*23*)	NbF_5 (*50*)
Se—F (terminal)	1.73	1.66	1.73	
Se · · · F (bridge)	2.35	2.43		
Nb—F (terminal)	1.78	1.82		1.77
Nb · · · F (bridge)	2.00	1.90		2.06

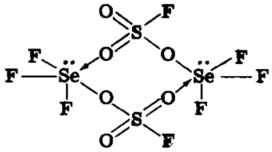


FIG. 4. Suggested structure of the dimer of $SeF_4 \cdot SO_3$. From Gillespie and Whitla (*81*).

the seleno analog to OPF_3, i. e., involving no Se—F bond. $SePF_3$ has also been prepared in a high-pressure reaction (300°C, 4000 atm) from selenium and PF_3 (*89*).

3. *Organic Derivatives of SeF_4*

Several diorganoselenium difluorides have been prepared and characterized (*81*) via the general reaction of Eq. (4):

$$2AgF_2 + R_2Se \rightarrow R_2SeF_2 + 2AgF \tag{4}$$

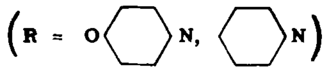
with R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, C_6H_5, or $(CH_2)_4$, carried out in Freon 113, yielding up to 87% of the fluorinated products. The diaryl- and dialkylselenium difluorides are monomeric in benzene solution. The NMR data were interpreted in terms of a trigonal-bipyramidal structure, with the fluorine atoms occupying the apical positions. Coupling between ^1H and ^{19}F, as well as between ^{77}Se and ^{19}F, was observed. The vibrational spectrum of $(CH_3)_2SeF_2$ and its deuterated analog has been reported, the results being compatible with C_{2v} symmetry of the molecule (*105, 192*).

The temperature dependence of the ^1H-NMR spectrum of dimethyl-, diethyl-, and diisopropylselenium difluoride and the ^{19}F-NMR spectrum of diisopropylselenium difluoride have been studied. With increasing size of the alkyl group, the rate of fluorine exchange has been found to increase. In addition, the F-exchange rate in the diorganoselenium difluorides investigated was independent of concentration within the range studied (*193*), quite contrary to SF_4 and SeF_4, for which exchange appears to occur principally via a second-order associative mechanism (*124*).

$(CH_3O)_3SeF$ has been prepared from $(CH_3O)_3SeCl$ and AgF in acetonitrile (*140*). The compound, a colorless liquid, is unstable at room temperature and decomposes extensively when distilled ($bp_{14} \sim 78°C$), according to Eq. (5):

$$(CH_3O)_3SeF \rightarrow (CH_3)_2SeO + CH_3F \tag{5}$$

Several aminoselenium fluorides of the type $RSeF_3$ and R_2SeF_2



have been prepared by reacting SeF_4 with the corresponding silylated amines $RSi(CH_3)_3$. Morpholinoselenium trifluoride (mp 105–107°C), piperidinoselenium trifluoride, dimorpholinoselenium difluoride (mp 132–134°C), and dipiperidinoselenium difluoride have been identified by chemical analysis. The respective studies do not give any structural data (*45*).

4. *Perfluoroalkyl Derivatives of SeF_4*

Perfluoroalkyl derivatives of SeF_4 of the general formula $RSeF_3$ ($R = CF_3, C_2F_5, p\text{-}CF_3C_6F_4$) and R_2SeF_2 ($R = CF_3, C_2F_5$) have been prepared (*78, 108, 110*). All are stable liquids at room temperature in Kel–F vessels, although they react with glass, with the trifluorides reacting most vigorously. CF_3SeF_3 was prepared (*110*) according to Eq. (6):

$$CF_3SeSeCF_3 + 2BrF_3 \rightarrow 2CF_3SeF_3 + Br_2 \qquad (6)$$

$C_2F_5SeF_3$ is formed quantitatively in the reaction of $(C_2F_5)_2Se_2$ with ClF between −130 and −22°C (*108*). Like SeF_4, it forms 1:1 adducts with CsF as well as with SbF_5.

$(CF_3)_2SeF_2$ and $(C_2F_5)_2SeF_2$ have been prepared by the reaction of the corresponding bis(perfluoroalkyl) monoselenide with ClF at room temperature, yielding quantitatively the products according to Eq. (7), where $R_f = CF_3, CF_5$:

$$(R_f)_2Se + 2ClF \rightarrow (R_f)_2SeF_2 + Cl_2 \qquad (7)$$

The compounds are also stable colorless liquids at room temperature, with vapor pressures of ~25 and 35 torr. $(C_2F_5)_2SeF_2$ does not form a complex with CsF; however, 1:1 adducts are formed with AsF_5 and SbF_5.

The ^{19}F-NMR and vibrational spectra of the perfluoroalkyl derivatives of SeF_4 are compatible with a trigonal-bipyramidal structure in the gaseous and liquid phases, the R_f groups preferentially occupying equatorial positions (Fig. 5). $(C_2F_5)_2SeF_2$ (I) is clearly associated in the liquid phase. The compound $CsF\cdot C_2F_5SeF_3$ appears to be ionic, i.e., $(C_2F_5SeF_4)^- Cs^+$ (III). The cation $[(C_2F_5)_2SeF]^+$ (IV), as indicated from these structural investigations, is fluorine-bridged to the corresponding counterions (AsF_6^-, SbF_6^-) (*108*).

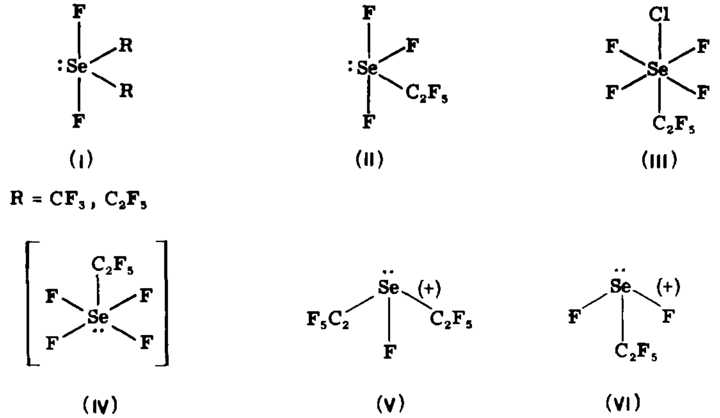


FIG. 5. Suggested structures of perfluoroalkyl derivatives of SeF_4. From Lau and Passmore (*108*).

B. TeF_4

The preparation of TeF_4 without the use of elemental fluorine has recently been reinvestigated. The reactions of elemental tellurium or TeO_2 with some inorganic fluorides, as well as the thermal decomposition of alkali pentafluorotellurate(IV) complexes, were studied in particular (*123*). In the fluorination experiments, i.e., CuF_2 or FeF_3 reacting with Te or TeO_2 (700–800°C), the best yields were obtained with FeF_3 plus TeO_2. Thermal decomposition of $NaTeF_5$ or $KTeF_5$ between 450 and 900°C produces TeF_4, only slightly contaminated with alkali fluorides. Attempts to prepare the presumably less stable complex $LiTeF_5$ were unsuccessful.

TABLE VIII

PHYSICAL PROPERTIES OF TeF_4[a]

Property		Ref.
Heat of vaporization (cal mol^{-1})	8174	*99*
Entropy of vaporization (eu)	12.62	*99*
Heat of fusion (cal mol^{-1})	6351	*99*
	3020	*28*
Entropy of fusion (eu)	15.77	*99*
Standard heat of formation, ΔH_f° (298°C) (kcal mol^{-1})	−246.7	*30*
	−248.3	*30*
Heat capacity, C_{p_s}, 298–402° (cal K^{-1} mol^{-1})	30	*28*

[a] See also Table III.

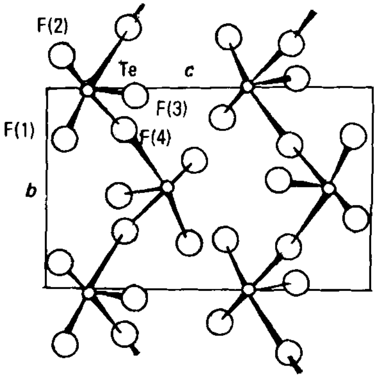


FIG. 6. Atomic arrangement in TeF_4, showing the projection down (100). From Edwards and Hewaidy (*54*).

Table VIII lists some of the more important physical properties of TeF_4. In the orthorhombic crystals, each tellurium atom is surrounded by three terminal and two bridging fluorine atoms, arranged at the apices of a distorted square pyramid. The square-pyramidal units are linked by cis-bridging atoms into endless chains with a bridge angle of 159°. The nearest intermolecular contacts to the tellurium atom are 2.94 and 3.10 Å, so that there are no other significant interactions. This geometry is in accordance with the steric activity of the lone electron pair at the tellurium atom. Figure 6 shows the atomic arrangement (*54*).

The vibrational spectrum of TeF_4 has been studied extensively, including matrix-isolation techniques (*2*). The most dilute matrices reveal absorptions attributable only to the monomeric TeF_4 molecule, with C_{2v} symmetry. The more concentrated matrices contain absorptions arising from several dimeric or oligomeric species (*2*).

1. TeF_4 and Lewis Acids

TeF_4 and SbF_5 form a 1:1 adduct (*16*). The Raman spectrum of this complex in the molten state has been recorded (*65*). It was not possible, however, to decide between the most plausible alternatives, i.e., ionization into the ions $(TeF_3)^+$ and $(SbF_6)^-$, or the formation of a fluorine-bridged structure $F_3TeFSbF_5$.

TeF_4 dissolves in excess SbF_5 by warming to ~100°C. From the white residue, after removal of the excess SbF_5 under vacuum at room temperature, two types of crystals could be grown. The bulk of the material consisted of very thin plates, unsuitable for crystallographic investiga-

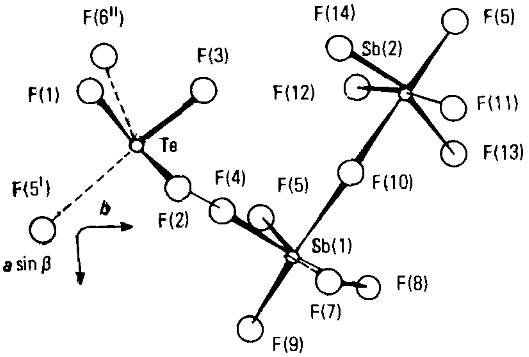


FIG. 7. Atomic arrangement in $TeF_4 \cdot 2SbF_5$, showing the projection down (001). From Edwards and Taylor (*56*).

tions, and was assumed to be $TeF_4 \cdot SbF_5$. A single block crystal could be isolated and grown for X-ray investigation, proving to be $TeF_4 \cdot 2SbF_5$ (*56*).

$TeF_4 \cdot 2SbF_5$ crystallizes in the monoclinic system. In the atomic arrangement (Fig. 7), the nearest fluorine atom neighbors to the tellurium and antimony atoms define the ions $(TeF_3)^+$ and $(Sb_2F_{11})^-$. However, interionic fluorine bridging leads to a complex, three-dimensional structural network. The $(TeF_3)^+$ ion has C_{3v} symmetry. Table IX gives the average distances and angles compared to related species (*56*).

2. *TeF₄ and Lewis Bases*

Crystalline salts of the general formula $MTeF_5$ have been prepared either from TeO_2 and the corresponding fluorides (M = Na, K, Rb, Cs, NH_4, C_5H_5NH, *n*-Bu_4N, Me_4N, Et_4N) or from KF and TeF_4 in aqueous

TABLE IX

AVERAGE BOND DISTANCES AND ANGLES IN TeF_3^+ AND RELATED SPECIES

Species	Mean M—F (Å)	Mean $\widehat{\text{F—M—F}}$ (deg)	Mean M · · · F bridge (Å)	(M · · · F)/(M—F)	Ref.
SF_3^+	1.496	97.47	2.614	1.75	*52*
SeF_3^+	1.66	94.2	2.43	1.46	*16*
TeF_3^+	1.84	90.3	2.59	1.41	*56*
SbF_3	1.92	87.3	2.61	1.36	*12*

hydrofluoric acid. Attempts to prepare $LiTeF_5$ from LiF and TeF_4 melts have been unsuccessful (*123*).

The only conclusive evidence concerning the structure of the TeF_5^- ion in solution is based on the ^{19}F-NMR spectrum of the n-Bu_4N^+ salt in CH_2Cl_2 at −50°C (*121*). Not only was the expected AB_4 pattern for the coupling of the fluorine atoms observed, but also coupling between ^{125}Te and ^{19}F, as well as ^{123}Te and ^{19}F. Asprey and Matwiyoff (*10*) reported ^{19}F-NMR spectra in the system $TeF_4/Bu_2NH_2F/CH_2Cl_2$, but observed no coupling. Obviously, a fast fluorine exchange between free F^- and TeF_5^- ions takes place in this system, which in fact could be confirmed by addition of n-Bu_4NF to n-Bu_4NTeF_5/CH_2Cl_2 (*121*).

Infrared and Raman spectra of powdered samples (*4, 84, 97, 121*) as well as single-crystal Raman studies (*4*) were applied to clarify the exact structure of the TeF_5^- entity in various salts. While earlier studies (*84*) based the assignments on a C_{4v} symmetry of the ion ($KTeF_5$), more recent investigations emphasize a C_s site symmetry (*97, 121*) in accordance with the results of three-dimensional single-crystal X-ray diffraction studies ($CsTeF_5$) (*97*).

Two almost simultaneous three-dimensional single-crystal X-ray diffraction studies of $KTeF_5$ (*55, 117*) yielded comparable results. The orthorhombic crystals contain isolated TeF_5^- ions which approximate to a square pyramid, but which in fact have only the C_s symmetry required by the space group (*Pbcm*).

$CsTeF_5$ also crystallizes in the orthorhombic system (*97, 98*). An infrared and Raman study (*97*) further confirmed the lowering of the symmetry of the TeF_5^- ions to C_s, in accordance with the strong quad-

TABLE X

DISTANCES AND ANGLES IN THE ISOELECTRONIC SPECIES SbF_5^{2-}, TeF_5^-, IF_5, AND XeF_5^+

	SbF_5^{2-}			TeF_5^-				
Species[a]	Na_2SbF_5 (*96*)	K_2SbF_5 (*117*)	$(NH_4)_2SbF_5$ (*27*)	TeF_4 (*54*)	$KTeF_5$ (*117*)	$CsTeF_5$ (*97*)	IF_5 (*95*)	XeF_5^+ (*15*)
$X—F_{ax}$	2.01	2.00	1.92	1.80	1.86	1.81	1.82	1.81
$X—F_{eq}$	2.08	2.04	2.08	2.03	1.95	1.93	1.87	1.88
$F_{ax}—F_{eq}$	2.56		2.55	2.52	2.42	2.40	2.40	
$F_{eq}—F_{eq}$	2.87		2.89	2.85	2.71	2.69	2.62	
$\widehat{F_{ax}—X—F_{eq}}$	77.7	83.0	79.4	81.8	78.9	79.8	80.9	80.0
$\widehat{F_{eq}—X—F_{eq}}$	87.2		88.0	88.8	87.8	88.2	88.6	

[a] Distances in angstroms; angles in degrees.

rupole splitting of the ^{125}Te-Mössbauer spectrum of $CsTeF_5$ (*79*) which also must be interpreted as a sign of strong deformation of the TeF_5^- ion. Table X gives a comparison of molecular parameters in the isoelectronic species SbF_5^{2-}, TeF_5^-, IF_5, and XeF_5^+ (*97*).

No experimental evidence could be obtained for the existence of the TeF_6^{2-} anion, despite extensive attempts to synthesize this species by a wide variety of reactions (*79*). The results reported by Shpinel *et al.* (*166*), assuming the formation of this ion in frozen solutions of TeO_2 and CsF in aqueous HF (in the stoichiometric proportions required), were shown to be basically similar to those of the solid $KTeF_5$. It is clearly quadrupole split, although by analogy with other hexahalogenotellurate(IV) complexes it should be unsplit (*79*).

3. *Organic Derivatives of TeF_4*

Some TeF_4 complexes with trimethylamine, dioxane, bipyridil, and tetramethylenediamine have been prepared, and their infrared spectra recorded (*85*). The complexes appear to be ionic. With monodentate ligands L, they can best be formulated as $(L_2TeF_3)^+(TeF_5)^-$. The stereochemistry of the cations is based on a pseudo-octahedral arrangement of the three fluorine atoms and the donor molecules around the tellurium, with a nonbonding pair of electrons occupying the sixth position. Adducts with bidentate ligands L^+ have the stoichiometry $L^+(TeF_4)_2$ and should be formulated as $(L^+TeF_3)^+(TeF_5)^-$.

Some aryltellurium di- and trichlorides react with AgF to form Ar_2TeF_2 and $ArTeF_3$, respectively (Ar = *p*-$MeOC_6H_4$, *p*-$EtOC_6H_4$) (*17*). The ^{1}H-NMR spectra of these compounds show the four-line AA′BB′ signal, characteristic of 1,4-disubstituted benzenes. All the aryltellurium compounds are soluble in DMSO.

4. *Perfluoroalkyl Derivatives of TeF_4*

$C_2F_5TeF_3$ and $(C_2F_5)_2TeF_2$ are the only perfluoroalkyl derivatives reported so far (*46*). $C_2F_5TeF_3$, a white solid (mp ~95°C), is formed in the reaction of $(C_2F_5)_2Te$ with ClF in the ratio 1:6 at −78°C, besides traces of *trans*-$C_2F_5TeClF_4$ and $TeClF_5$, compounds to which $C_2F_5TeF_3$ is further converted by excess ClF at room temperature. It forms adducts with CsF, and also reacts with SbF_5 to yield $C_2F_5TeF_3 \cdot 2SbF_5$. $(C_2F_5)_2TeF_2$ is a liquid (mp ~4°C), resulting from the reaction of $(C_2F_5)_2Te$ with ClF in a 1:2 ratio at −78°C. It forms 1:1 adducts with CsF as well as with SbF_5. No structural data have been reported.

IV. Oxide Fluorides of Se(IV) and Te(IV)

A. $SeOF_2$

A reinvestigation of very pure $SeOF_2$ (impurity calculated 1.8% mole fraction) gave a melting point of 15.01°C, $\Delta H_{fus} = 1.93 \pm 0.05$ kcal mol^{-1}, and $\Delta H_{vap} = 11.2 \pm 0.2$ kcal mol^{-1} (*29*). The hydrolysis reaction of $SeOF_2$ with NaOH according to Eq. (8) formed the basis for a determination of $\Delta H^{\circ}_{f298^\circ} = -137.2 \pm 3.8$ kcal mol^{-1} (*30*).While observing the formation of this compound in the reaction of ClF with SeO_2, the ^{19}F-NMR spectrum of $SeOF_2$ was recently recorded [$\delta(CCl_3F) = -38.6$ ppm] (*107*).

$$SeOF_{2(l)} + 4NaOH_{(aq)} \rightarrow Na_2SeO_{3(aq)} + 2H_2O_{(l)} \qquad (8)$$

The microwave spectrum of $SeOF_2$ served for an extended analysis of the structure of this molecule. The following parameters have been deduced: $r_{SeO} = 1.576$; $r_{SeF} = 1.7295$ Å; $\widehat{FSeF} = 92.22°$; $\widehat{OSeF} = 104.82°$. The dipole moment is 2.84 D along an axis at an angle of 50.30° to the SeO bond and in the plane that contains this bond and bisects the FSeF angle (*22*).

1. *$SeOF_2$ and Lewis Acids*

$SeOF_2$ reacts with NbF_5, yielding colorless needles of the composition $SeOF_2{\cdot}NbF_5$ (*51*). The atomic arrangement is reproduced in Fig. 8, and the interatomic distances and angles are given in Table XI. The bridging atom has been assumed to be oxygen by analogy with the $SeOCl_2{\cdot}SbCl_6$ adduct (*94*), since it cannot be distinguished from fluorine by X-ray methods. While Nb is at the center of a somewhat distorted octahedron with approximately C_{4v} symmetry, three inter-

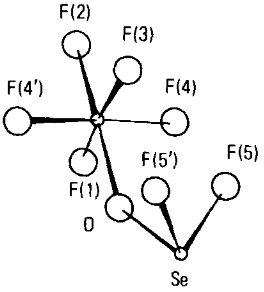


FIG. 8. Atomic arrangement in $SeOF_2{\cdot}NbF_5$. From Edwards and Jones (*51*).

TABLE XI

DISTANCES AND ANGLES IN $SeOF_2$ AND $SeOF_2 \cdot NbF_5$

Species	$SeOF_2$[a] (vapor)	$SeOF_2 \cdot NbF_5$[b] (adduct)
Se—F (Å)	1.7295	1.68
Se—O (Å)	1.576	1.60
$\widehat{\mathrm{F{-}Se{-}F}}$ (deg)	92.22	92.6
$\widehat{\mathrm{F{-}Se{-}O}}$ (deg)	104.82	99.7

[a] From Bowater *et al.* (*22*).

[b] From Edwards and Jones (*51*).

molecular Se—F contacts complete a much distorted octahedral coordination around selenium

2. *$SeOF_2$ and Lewis Bases*

$KSeOF_3$, together with related complexes of the general formula $M(SeOX_3)$ ($X = F, Cl, OCH_3, OC_2H_5$), were prepared and investigated by studying their infrared and Raman spectra (*131*). $KSeOF_3$ (mp 138°C) is formed exothermally from KF in excess $SeOF_2$. At about 400°C, a reverse decomposition starts. The spectra are interpreted as confirming the expected geometry with two fluorine atoms at the apices of a pseudo-trigonal bipyramid, in agreement with the predictions of the VSEPR theory (*80*).

B. SeOClF

While studying various systems involving selenium compounds, some NMR evidence for the formation of SeOClF in a mixture of $SeOCl_2$ and $SeOF_2$ has been obtained (*18*).

C. SeO_2F^- AND $SeO_2F_2^{2-}$

$KSeO_2F$, originally prepared from SeO_2 and KF and investigated by Paetzold and Aurich (*130*), was reinvestigated recently and its infrared and Raman spectra compared with the spectrum of the isoelectronic molecule BrO_2F (*83*). The salt was made either by heating equimolar amounts of KF with SeO_2 or by shaking a suspension of the starting materials in DMSO. $CsSeO_2F$ can also be prepared from the components in liquid SO_2 (*145*). An assignment of the spectral lines in agreement with an assumed C_s symmetry is presented which confirms analogies with BrO_2F, $SeO_2(OH)^-$, and SO_2F^- (*83*).

The aforementioned frequencies have been used for a force-constant calculation (*13*). The bond orders deduced with the simple method of Siebert (*167*) are 0.63 for the Se—F bond and 1.5 for the Se—O bond. These values also prove a general similarity to BrO_2F and ClO_2F. The low value of the Se—F force constant and high value of the corresponding mean vibrational amplitude, as well as its large temperature dependence, are attributed to a large ionic character and also point to the possibility of some fluorine bridging in the crystal lattice, as suggested earlier (*130, 167*).

$K_2SeO_2F_2$ (always containing some $KSeO_2F$) forms at 300°C in a melt of excess KF with SeO_2. The Raman spectrum of the salt is consistent with $SeO_2F_2^{2-}$ having C_{2v} symmetry, similar to $ClO_2F_2^-$, $IO_2F_2^-$, and $TeO_2F_2^{2-}$ (*83*).

D. Te(IV) OXIDE FLUORIDES

1. $M_2TeO_2F_2$ ($MTeO_2F$) and M_2TeOF_4

$$TeO_2 + MTeF_5 + 3MF \rightarrow 2M_2TeOF_4 \qquad (9)$$

$CsTeOF_4$ and $KTeOF_4$ were prepared according to Eq. (9) by heating the components in a platinum boat to 550°C. No reaction was observed on refluxing the starting materials for 24 hours in DMSO. $Cs_2TeO_2F_2$ and $Rb_2TeO_2F_2$ could be obtained from MF and TeO_2 in the ratio 2:1 by heating to 800°C (*119*). No compounds of the type $M(I)TeO_2F$ (M = Cs, Rb) could be obtained, quite contrary to the behavior of SeO_2 which readily reacts to yield $M(I)SeO_2F$ (*130*).

The potassium salts of the isoelectronic anions SbF_5^{2-} and $TeOF_4^-$ are isomorphous, according to X-ray powder photography. This is also true for the cesium salts. An assignment of the vibrational spectrum confirms the basic C_{4v} symmetry and the prediction of VSEPR theory (*80*) that the oxygen atom is axial. The vibrational spectra of $M_2TeO_2F_2$ compounds show evidence of oxygen bridging. The spectra are compatible with C_{2v} symmetry, with the oxygens in equatorial positions.

2. $H_2Te_2O_3F_4$

In 1976, an X-ray powder diffraction analysis of a substance obtained from TeO_2, dissolved in concentrated hydrofluoric acid, was performed (*96*). The orthorhombic crystals had the composition $H_2Te_2O_3F_4$. The structure was shown to be characterized by

$(OTeF_2—O—TeF_2O)^{2-}$ anions, which are linked by hydrogen bonds (O—H · · · F) to form a very distorted diamond network. Each tellurium atom is at the center of a much distorted trigonal bipyramid, with two axial fluorine atoms. The nonbonding electron pair, as well as two oxygen atoms (one of them bridging two tellurium atoms), take up the equatorial positions. The distances (Å) derived are: Te—O (—H · · ·), 1.896; Te—O— (bridged), 1.919; Te—F (terminal), 1.931; Te—F (· · · H-bridged), 2.012; O—H, 1.0; H · · · F, 1.6. The angles are: Te—$\widehat{\mathrm{F}}$—Te, 120°; F—$\widehat{\mathrm{Te}}$—F, 158.3°; and O—$\widehat{\mathrm{Te}}$—O, 95.9°.

3. *Mössbauer Spectra of Te(IV) Oxide Fluorides*

A study of the general features of the isomer shifts and quadrupole splittings in the ^{125}Te-Mössbauer spectra of $K_2TeO_2F_2$, $Cs_2TeO_2F_2$, $CsTeOF_4$, and $KTeF_5$, together with a number of Te(IV) oxides, has been undertaken (*47*). The results are explained in terms of about 10% s-character in the bonding orbitals. A description of the bonding in these compound in the form of sp^3, sp^3d, and sp^3d^2 hybrids would overemphasize the role of the 5s-electrons in the bonding.

V. Hexahalides

A. SeF_6 AND TeF_6

The six fundamental vibrational frequencies for SeF_6 and TeF_6 are given in Table XII (*21, 37, 38, 103*). Force constants for SeF_6, calculated with the frequencies from vapor-phase Raman spectra (*21*) and using isotope shifts and Coriolis coupling constants as additional data (*103*), are listed in Table XIII in comparison to TeF_6 (*1, 24, 104, 125, 139*).

Vapor-phase intensity studies of the Raman-active bands of SeF_6 and TeF_6 yielded, via electrooptical parameters, a Pauling covalent bond character of Se—F = 0.60 and Te—F = 0.47, and Pauling elec-

TABLE XII

FUNDAMENTAL VIBRATIONAL FREQUENCIES (cm^{-1}) FOR SeF_6 AND TeF_6 IN THE VAPOR PHASE[a]

	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_3(f_{1u})$	$\nu_4(f_{1u})$	$\nu_5(f_{2g})$	$\nu_6(f_{2u})$
SeF_6	708.0	658.3	779.3	435.3	402.5	263.5
TeF_6	697.6	671.5	751.5	326.5	312.3	201.0

[a] From refs. (*21, 37, 38, 103*).

TABLE XIII

FORCE CONSTANTS FOR SeF_6 AND TeF_6 (mdyn $Å^{-1}$)^a

Force constant	SeF_6	TeF_6
$F_{11}(a_{1g})$	5.61	5.50
$F_{22}(e_g)$	4.85	5.08
$F_{33}(f_{1u})$	4.93	4.78–4.98
$F_{34}(f_{1u})$	0.46	0.01–0.24
$F_{44}(f_{1u})$	0.646	0.40
$F_{55}(f_{2g})$	0.453	0.27
$F_{66}(f_{2u})$	0.389	0.22
f_r	5.02	4.99–5.11
f_{rr}	0.13	0.07
f_{rr}'	0.09	0.009–0.05

^{a} Refs. (*1, 24, 104, 125, 139*).

tronegativity for Se = 2.55 and Te = 2.25 (*38*). From molecular-beam studies of the reactions of K and Cs with SeF_6 and TeF_6, electron affinities (eV) of SeF_6 = 3.0 and TeF_6 = 3.3 have been derived (*8, 42*). Electron diffraction data on TeF_6 have been reanalyzed and yielded a Te—F distance at 20°C of 1.815 Å (*86*), compared with a value for Se—F in SeF_6 of 1.688 Å (*66*). The formation and properties of the transient species SeF_6^- and TeF_6^- have been investigated (*20, 93 122, 184*). Charge-transfer interactions of SeF_6 and TeF_6 with aromatic hydrocarbons and fluorocarbons have also been demonstrated (*90–92*).

1. *Hydrolysis of SeF_6 and TeF_6*

Hydrolysis of TeF_6 occurs stepwise via fluoroorthotelluric acids, $Te(OH)_nF_{6-n}$ (n = 1–5), which possess considerable stability in the resulting equilibrium mixture (*57, 67*). By means of ^{19}F-NMR spectroscopy, most of the possible stereoisomers of these acids have been detected. With the exception of $HOTeF_5$, prepared by a different route (*61*), none of the hydrolysis products has been isolated so far. $HOTeF_5$ hydrolyzes stepwise as well, a separation of the products being possible by paper chromatography (*61, 101*). Alternatively, by reacting orthotelluric acid, $Te(OH)_6$, with HF (40% or AHF), up to four hydroxy groups can be replaced by fluorine (*57, 101*).

In contrast to TeF_6, mixtures of SeF_6 and H_2O appear not to interact over long time intervals at room temperature (*57*). $HOSeF_5$ and possibly $HSeO_3F$, however, are detected by ^{19}F-NMR spectroscopy in solutions of selenic acid in AHF (*57*).

2. *Alcoholysis of* TeF_6

The reaction of TeF_6 with alcohols in the presence of sodium fluoride or pyridine as HF acceptors yields a variety of mono-, di-, and trialkoxotellurium(VI) fluorides (*39, 44, 68–70, 72*):

$$TeF_6 + nROH = TeF_{6-n}(OR)_n + nHF \tag{10}$$

With sodium alkoxide, up to five fluorines can be substituted in TeF_6. Alternatively, oxidative fluorination of $Te(OR)_4$ affords the corresponding difluorotellurium(VI) species $TeF_2(OR)_4$ (*70*).

$F_5TeO(CH_2)_2OTeF_5$, *cis*-$[O(CH_2)_2O]TeF_4$, and related compounds are formed in reactions of TeF_6 with ethylene glycol and other polyhydric alcohols (*69*). The alkoxotellurium(VI) fluorides isolated so far are distillable liquids with considerable stability against hydrolysis. Some of these compounds have been prepared more easily by reacting diazoalkanes with pentafluoroorthotelluric acid (*174*), as in Eq. (11):

$$RCHN_2 + HOTeF_5 = N_2 + RCH_2OTeF_5 \tag{11}$$

In contrast to alcohols, trimethyl- and triphenylsilanol react with TeF_6 to form the corresponding fluorosilane and pentafluoroorthotelluric acid (*71*). The system TeF_6–ROH has also been studied by reacting $Te(OCH_3)_6$ with anhydrous hydrogen fluoride [Eq. (12)].

$$Te(OCH_3)_6 + nHF = Te(OCH_3)_{6-n}F_n + nCH_3OH \tag{12}$$

Evidence for the existence of most of the possible substitution products has been obtained by ^{19}F-NMR spectroscopy (*3*).

3. $TeF_5(NR_2)$, $TeF_4(NR_2)_2$, *and Related Compounds*

Cleavage reactions of the silicon–nitrogen bond of silylamines by TeF_6 affords aminotellurium(VI) fluorides (*73, 74, 76*) as in Eq. (13), where $n = 1, 2$:

$$nR_2N\text{—}Si(CH_3)_3 + TeF_6 = TeF_{6-n}(NR_2)_n + nFSi(CH_3)_3 \tag{13}$$

The dialkylaminotellurium(VI) pentafluorides are pale yellow liquids that decompose rapidly above 35°C. Bis(dimethylamino)tellurium(VI) tetrafluoride is a pale yellow solid, mp 57°C. The compounds have been characterized by IR, Raman, ^1H-NMR, ^{19}F-NMR, and mass spectroscopy. Reaction of $(R_3Si)_2NH$ with TeF_6 produces $R_3SiNHTeF_5$ (mp 9°C), which can be cleaved with HF to yield aminotellurium(VI) pentafluoride (*155*) [Eq. (14)].

$$R_3SiNHTeF_5 + HF = R_3SiF + H_2NTeF_5 \tag{14}$$

H_2NTeF_5 (mp 82.5°C, bp 121°C) exhibits acid as well as base behavior: a 1:1 adduct is formed with AsF_5, and cleavage of $R_3SiNHTeF_5$ with CsF affords $Cs^+NHTeF_5^-$ (*155*).

The experimental finding that predominantly cis products are formed in various disubstitution reactions on TeF_6 has been explained on the basis of an MO study (*9*).

4. TeF_7^- and TeF_8^{2-}

The reaction of TeF_6 with CsF and RbF was reinvestigated with C_6F_6 as solvent (*148*). With CsF, a limiting composition of $CsF \cdot TeF_6$ is approached, while RbF gives a compound of composition $2RbF \cdot TeF_6$. These materials are stable in the solid state only. The IR and Raman spectra have been tentatively interpreted in terms of D_{5h} and D_{4d} structures for the TeF_7^- and TeF_8^{2-} anions, respectively.

5. $Te(OH)_6 \cdot NaF$ and $Te(OH)_6 \cdot 2KF$

$Te(OH)_6$ forms adducts with alkali-metal fluorides such as $Te(OH)_6 \cdot NaF$ or $Te(OH)_6 \cdot 2KF$ (*102*). Single-crystal X-ray diffraction shows that, contrary to the earlier assumption, there is no direct bonding of fluorine to tellurium. The fluoride ions are incorporated into the structure by short O—H · · · F hydrogen bonds (*6, 7*).

B. SeF_5Cl, TeF_5Cl, AND TeF_5Br

SeF_5Cl (mp −19°C, bp 4.5°C), first obtained from SeF_4 and ClF (*41*), is best prepared from $CsSeF_5$ and $ClOSO_2F$ (*144*), as in Eqs. (15). TeF_5Cl (mp −28°C, bp 13.5°C), first obtained from $TeCl_4$ and F_2 using a flow method at 25°C (*75*), is more conveniently prepared by reacting ClF with TeF_4, $TeCl_4$, or TeO_2 (*106*). TeF_5Br has only been detected in

TABLE XIV

STRETCHING FORCE CONSTANTS (mdyn Å^{-1}) FOR SeF_5Cl[a] AND TeF_5Cl[b]

Constant	SeF_5Cl	TeF_5Cl
f_R	4.42	4.93
f_r	4.31	4.76
f_D	2.75	2.86

[a] From Christe *et al.* (*36*).

[b] From Brooks *et al.* (*24*).

the fluorination of $TeBr_4$ by its ^{19}F-NMR spectrum (*75*). Normal coordinate analyses were carried out for SeF_5Cl and TeF_5Cl (Table XIV) (*24, 36, 183*). In both cases, there is a decrease of the stretching-force-constant values from MF_6 to MF_5Cl. Obviously, the substitution of one fluorine atom in MF_6 by the less electronegative chlorine atom causes an increased polarity of the remaining M—F bonds. Only for TeF_5Cl have molecular parameters been reported, derived from microwave spectral analysis (*109*): Te—Cl, 2.250 Å; and, if equality of axial and equatorial Te—F distances is assumed, Te—F measures 1.830 Å and the angle (F_{ax}—Te—F_{eq}) is 88° 15′.

$$\begin{gathered} CsF + SeF_4 = CsSeF_5 \\ CsSeF_5 + ClOSO_2F = SeF_5Cl + CsOSO_2F \end{gathered} \tag{15}$$

VI. Chemistry of the F_5SeO and F_5TeO Groups

The F_5SeO group, and especially the F_5TeO group, can best be characterized as pseudohalogens or, more specifically, as pseudofluorines. After the discovery of pentafluoroorthotelluric acid, $HOTeF_5$ (*59, 61*), it soon became clear that the chemistry of the F_5TeO group is almost as extensive as that of fluorine. This is especially illustrated by the stability of xenon(II) pentafluoroorthotellurates (*168–173*). Exceptions, with no corresponding F_5TeO or F_5SeO compounds known so far, appear to be only KrF_2 and some high-oxidation-state compounds such as ClF_5, IF_7, or PtF_6. The preparation of pentafluoroorthoselenic acid, $HOSeF_5$ (*149*), then allowed most of the chemistry achieved with the F_5TeO group as a ligand to be duplicated.

The similarity to fluorine as a ligand, and especially the ability of the F_5SeO and F_5TeO groups to form the most stable xenon compounds besides the simple fluorides, is certainly associated with high group electronegativities. Using the Dailey–Schoolery or Cavanough–Dailey equations (*32, 43*) for calculating group electronegativities from ^1H-NMR data of the corresponding ethyl compounds (C_2H_5F, $C_2H_5OTeF_5$), a group electronegativity of 3.87 for the F_5TeO group in comparison to 3.95 for fluorine, is obtained (*176*). A rationale for this high electronegativity is certainly the inductive effect of the five fluorines, thus additionally promoting $(pd)\pi$ back-bonding from oxygen to the chalcogen.

In contrast to fluorine, however, the F_5SeO and F_5TeO groups are strictly monodentate ligands with no further tendency for fluorine or oxygen bridging. This usually leads to relatively low-melting or low-boiling compounds, despite high molecular weights, and to a good solu-

TABLE XV

F_5SeO AND F_5TeO COMPOUNDS OF MAIN-GROUP ELEMENTS[a]

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
(Li, Na, K, Rb, Cs, NH_4)$^+$ F_5SeO^-, F_5TeO^- (*60,151,178*)		$B(OTeF_5)_3$ $B(OTeF_5)_4^-$ $L \cdot B(OTeF_5)_3$ (*177,179*) $Al(OTeF_5)_3$ (*176*)	$R—OTeF_5$ (R = alkyl) $Si(OTeF_5)_4$ $R_3SiOTeF_5$ $R_3GeOTeF_5$ $R_3SnOTeF_5$ (*175*) $R_3SiOSeF_5$ (*160*) $CF_3COOSeF_5$ (*152*) $CF_3COOTeF_5$ (*176*)	OPF_2SeF_5 (*164*) $As(OSeF_5)_3$ $Sb(OSeF_5)_3$ (*164*) $As(OTeF_5)_3$ (*175*) $SbF_n(OTeF_5)_{5-n}$ (*179*)	F_5TeOSO_2F F_5TeOSO_2Cl $(F_5TeO)_2SO_2$ F_5TeOSO_3H (*19,58,59,61*) F_5SeOSO_2F (*141*) $F_5SeOS_2O_5F$ (*152*) $AcOTe(OTeF_5)_3$ $AcOSe(OTeF_5)_3$ (*180*)	F_5SeOF (*120*) F_5SeOCl F_5SeOBr F_5SeOI $(F_5SeO)_3I$ (*153,154,157*) $(F_5SeO)_3Br$ $Br(OSeF_5)_4^-$ (*153,154*) F_5TeOCl (*165*) $F_4Se(OF)_2$ (*182*) $IF_n(OTeF_5)_{5-n}$ $I(OTeF_5)_5$ $OI(OTeF_5)_3$ $IF_n(OSeF_5)_{5-n}$ (*113*)	$Xe(OTeF_5)_2$ $FXeOTeF_5$ $XeOTeF_5^+$ (*168–173*) $Xe(OTeF_5)_4$ $Xe(OTeF_5)_6$ $OXe(OTeF_5)_4$ (*114,115*) $Xe(OSeF_5)_2$ $FXeOSeF_5$ (*150,156,157, 165,187*)

[a] References are given in parentheses.

TABLE XVI

F_5SeO and F_5TeO Compounds of Transition Metals[a]

IIIB	IVB	VB	VIB	VIIB	VIII	IB	IIB
	$Ti(OTeF_5)_4$ $Ti(OTeF_5)_6^{2-}$ $TiCl_n(OTeF_5)_{4-n}$ (*63,162,181*)	$OV(OSeF_5)_3$ (*162*)	$O_2Cr(OSeF_5)_2$ (*162*) $MoF_n(OTeF_5)_{6-n}$ $OMoF_n(OTeF_5)_{4-n}$ $WF_n(OTeF_5)_{6-n}$ (*180*) $ClW(OTeF_5)_5$ (*162*) $U(OTeF_5)_6$ $UF_n(OTeF_5)_{6-n}$ (*163,186*)			$AgOTeF_5$ (*118,178*)	$CH_3HgOTeF_5$ $Hg(OTeF_5)_2$ (*165,178*) $Hg(OSeF_5)_2$ (*151*)

---

[a] References are given in parentheses.

bility in apolar solvents. Tables XV and XVI give a listing of the pentafluoroorthoselenates and tellurates so far prepared.

A. PREPARATIVE METHODS FOR F_5SeO AND F_5TeO COMPOUNDS

In accord with the high acidities of $HOSeF_5$ and $HOTeF_5$, acid displacement reactions are frequently performed, affording ionic as well as covalent compounds as in Eqs. (16)–(18). For the preparation of alkoxopentafluoroorthotellurates, a method that is widely applied is the reaction of the respective alcohol with TeF_6 (Section V,A,2).

$$E{-}F + HOXF_5 = HF + E{-}OXF_5 \quad (\text{e.g., } XeF_2,\ HgF_2) \tag{16}$$

$$E{-}Cl + HOXF_5 = HCl + E{-}OXF_5 \quad (\text{e.g., } CsCl,\ TiCl_4,\ BCl_3,\ R_3SiCl) \tag{17}$$

$$E{-}CH_3 + HOXF_5 = CH_4 + E{-}OXF_5 \quad (\text{e.g., } R_4Sn,\ R_2Hg) \tag{18}$$

An extremely versatile reagent for transferring F_5TeO groups is boron tris(pentafluoroorthotellurate), $B(OTeF_5)_3$. Owing to its extraordinary Lewis acidity (*177*), a wide range of fluorides interacts with this compound, as in Eq. (19) (e.g., AsF_3, SbF_5, XeF_4, XeF_6, MoF_6, WF_6, UF_6):

$$E{-}F + B(OTeF_5)_3 = \tfrac{1}{3}BF_3 + E{-}OTeF_5 \tag{19}$$

Similar reagents, although more limited, are $R_3SiOTeF_5$ and $Hg(OSeF_5)_2$.

B. $HOSeF_5$ AND $HOTeF_5$

Pentafluoroorthotelluric acid, $HOTeF_5$ (mp 39.1°C, bp 59.7°C), is easily obtained in high yield from BaH_4TeO_6 (*62*) and $HOSO_2F$ (*26, 58, 59, 61*) as in Eq. (20):

$$BaH_4TeO_6 + 7HOSO_2F = HOTeF_5 + Ba(SO_3F)_2 + 5H_2SO_4 \tag{20}$$

Pentafluoroorthoselenic acid, $HOSeF_5$ (mp 37°C, bp 44°C), is best prepared from SeO_2F_2, $HOSO_2F$, and HF or KHF_2 as in Eq. (21) (*149, 151, 157, 165*):

$$SeO_2F_2 + 2HOSO_2F + KHF_2 = HOSeF_5 + KSO_3F + H_2SO_4 \tag{21}$$

Both compounds are strong acids, $HOSeF_5$ exhibiting higher oxidizing and fluorinating behavior than $HOTeF_5$. The pK_a value of 8.8 for $HOTeF_5$ in glacial acetic acid is in the range of sulfuric acid ($pK_a = 7.0$) and hydrogen chloride ($pK_a = 8.4$) (*135, 136, 142*).

TABLE XVII

STRETCHING FORCE CONSTANTS (mdyn Å^{-1}) FOR F_5SeO^- AND F_5TeO^-[a]

Constant	F_5SeO^-	F_5TeO^-
f_O	6.49	6.16
f_r	3.59	4.16
f_R	2.98	3.38

f_O: X—O stretch; f_r: X—F_{eq} stretch; f_R: X—F_{ax} stretch

[a] From Mayer and Sladky (*118*).

C. F_5SeO^- AND F_5TeO^-

Group IA salts containing the F_5SeO^- or F_5TeO^- anion are prepared by interaction of group IA chlorides or fluorides with the respective acids (60, 151, 178). (Cs, $NH_4)^+F_5SeO^-$ salts are cubic, adopting a NaCl lattice (*157*). (K, Rb, Cs, $NH_4)^+F_5TeO^-$ salts are rhombohedral, adopting the $KOsF_6$ structure, which is related to the CsCl lattice. From crystallographic data, an anion radius for F_5TeO^- is computed which shows this ion to be somewhat larger than an iodide ion (*178*).

A normal-coordinate calculation has been carried out for F_5SeO^- and F_5TeO^-, as shown in Table XVII (*118*). The values for the oxygen stretch, f_O, indicate for F_5XO^- bond orders somewhat smaller than 2 (f_O, SeO_2F_2 = 8.00 mdyn Å^{-1}). Obviously, resonance structures such as $F^-XF_4{=}O$ are dominant over $F_5X{-}O^-$, as expected from the higher electronegativity of fluorine against oxygen. This polarization of the X–F bond also explains the strong drop of f_{X-F} from XF_6 (f_{X-F} = 5) to F_5XO^-. Additionally, MO arguments favor a stronger polarization of the fluorine atom trans to oxygen, compared to the equatorial fluorine atoms, thus causing f_R to become smaller than f_r (*118*).

D. $F_5SeOSeF_5$ AND $F_5TeOTeF_5$

Bis(pentafluoroselenium) oxide, $F_5SeOSeF_5$ (mp −82.1°C, bp 55.2°C), is produced besides $F_5SeOOSeF_5$ by the reaction of fluorine with selenium dioxide (*141, 182*). Bis(pentafluorotellurium) oxide, $F_5TeOTeF_5$ (mp −36.6°C, bp 59.8°C) is prepared by the method shown in Eq. (22) (*58*). This compound has been obtained several times since 1933, but was always mistakenly characterized as Te_2F_{10}. The proposed existence of Te_2F_{10}, which in fact has not been prepared to date,

TABLE XVIII

MOLECULAR PARAMETERS OF $F_5SeOSeF_5$ AND $F_5TeOTeF_5$[a]

Parameter	$F_5SeOSeF_5$	$F_5TeOTeF_5$
X—O	1.70 Å	1.83 Å
$X—F_{eq}$	1.68 Å	1.82 Å
$X—F_{ax}$	1.66 Å	1.80 Å
Angle (XOX)	142°	145°
Angle ($F_{ax}XF_{eq}$)	88.9°	89.9°

[a] From Oberhammer and Seppelt (*126,127*).

is a common textbook error (*191*). Both compounds, though formal anhydrides of the corresponding acids, are quite resistant against hydrolysis.

$$(F_5TeO)_2SO_2 + CsF = F_5TeOTeF_5 + CsOSO_2F \qquad (22)$$

An electron diffraction study of $F_5SeOSeF_5$ and $F_5TeOTeF_5$ shows a high bridge angle which is larger in the tellurium compound, although steric hindrance diminishes in going from selenium to tellurium. The equatorial fluorine atoms have an eclipsed orientation. An explanation is given in terms of some (pd)π-bonding between oxygen and the chalcogen (*126, 127*). Molecular parameters are shown in Table XVIII.

E. $Se_2O_2F_8$, $Te_2O_2F_8$, AND OTHER TELLURIUM–OXYGEN–FLUORINE COMPOUNDS

$Se_2O_2F_8$ (mp −12°C, bp 65°C) and $Te_2O_2F_8$ (mp 28°C, bp 77.5°C) are prepared by pyrolysis of $NaOSeF_5$ and $LiOTeF_5$ or $B(OTeF_5)_3$, respectively (*128, 159, 160, 190*). The molecular structures of these two com-

TABLE XIX

MOLECULAR PARAMETERS OF $Se_2O_2F_8$ AND $Te_2O_2F_8$[a]

Parameter	$Se_2O_2F_8$	$Te_2O_2F_8$
X—O	1.78 Å	1.92 Å
$X—F_{eq}$	1.67 Å	1.80 Å
$X—F_{ax}$	1.70 Å	1.85 Å
Angle (XOX)	97.5°	99.5°
Angle (OXO)	82.5°	80.5°

[a] From Oberhammer and Seppelt (*128*).

TABLE XX

TELLURIUM–OXYGEN–FLUORINE COMPOUNDS

Compound	mp, °C	bp, °C	Ref.
$F_5TeOTeF_5$	−36.6	59.8	*58,127*
$F_5TeOOTeF_5$	−39	81.5	*165,171*
$Te_2O_2F_8$	28	77.5	*128*
trans-$F_4Te(OTeF_5)_2$	19	150	*112*
cis-$F_4Te(OTeF_5)_2$	−26.5	127	*112*
trans-$F_2Te(OTeF_5)_4$	76	110(33)	*138*
cis-$F_2Te(OTeF_5)_4$	−12	63(2)	*111,112*
$(TeF_4O)_n$		250	*177*
$FTe(OTeF_5)_5$	48	95(5)	*112*
$Te(OTeF_5)_6$	242.5	100(0.01)	*112*
$Te(OTeF_5)_4$	90	90(0.01)	*112*

pounds have been determined in the gas phase by electron diffraction (*128*). The skeleton of each molecule is a planar four-membered ring, formed by the two chalcogens and two bridging oxygen atoms. The compounds can be looked upon as the dimerization products of the unknown $OTeF_4$ and of $OSeF_4$, which has only a transitory existence (*158*), thus illustrating the instability of 5-fold coordinated Te(VI) and Se(VI). The more important molecular parameters are listed in Table XIX.

Other decomposition products of $B(OTeF_5)_3$ are $F_5Te(OTeF_4)_nOTeF_5$ ($n = 1$ to ~ 25) (*177*). The simplest members of this series *cis*- and *trans*-$F_4Te(OTeF_5)_2$, have also been obtained by the thermal decomposition of $Xe(OTeF_5)_2$ (*112, 171*). *cis*- and *trans*-$F_2Te(OTeF_5)_4$ are prepared by fluorination of $Te(OTeF_5)_4$ with fluorine. Further tellurium–oxygen–fluorine compounds have been synthesized by reacting $B(OTeF_5)_3$ with TeF_4, and $Te(OTeF_5)_4$ with XeF_2 or $Xe(OTeF_5)_2$; see

TABLE XXI

REACTIONS OF SeO_2F_2

Reagent	Product	Reference
$(RO)_2SeO_2$	$ROSeO_2F$	*132*
N_2O_3/N_2O_4 or HNO_3	NO^+, $NO_2^+SeO_3F^-$	*33,49*
$HF/HOSO_2F$	$HOSeF_5$	*149*
$(SeO_3)_4$	$Se_2O_5F_2$	*48*
$(SeO_2)_n$	$FSeO_2OSeOF$	*48*
$MHSeO_4$	$MSeO_3F$, $HOSeO_2F$	*33*
$NH_4SeO_3NH_2$	$NH_4N(SeO_2F)_2$	*143*

Table XX (*111, 112, 137, 138*). Most of these oxide–fluorides are quite stable against hydrolysis and rather volatile, despite high molecular weights.

VII. SeO_2F_2

SeO_2F_2 (mp −99°C, bp −8.4°C) is still best prepared from $BaSeO_4$ and fluoroselenic acid (*64*). It is a starting material for derivatives of fluoroselenic acid, shown in Table XXI. Fluoroselenates with the structure $F_2As(OSeO_2OAsF)_nOSeO_2F$ and related compounds are obtained in reactions of AsF_3 and SeO_3 (*189*).

REFERENCES

1. Abramovitz, S., and Levin, I. W., *J. Chem. Phys.* **44,** 3353 (1966).
2. Adams, C. J., and Downs, A. J., *Spectrochim. Acta, Part A* **28,** 1841 (1972).
3. Agranat, I., Rabinovitz, M., and Selig, H., *Inorg. Nucl. Chem. Lett.* **11,** 185 (1975).
4. Alexander, L. E., and Beatti, I. R., *J. Chem. Soc. A* p. 3091 (1971).
5. Alexander, L. E., and Beatti, I. R., *J. Chem. Soc. A* p. 1745 (1972).
6. Allmann, R., *Acta Crystallogr., Sect. B* **32,** 1025 (1976).
7. Allmann, R., and Haase, W., *Inorg. Chem.* **15,** 804 (1976).
8. Annis, B. K., and Datz, S., *J. Chem. Phys.* **66,** 4468 (1977).
9. Armstrong, D. R., Fraser, G. W., and Meikle, G. D., *Inorg. Chim. Acta* **15,** 39 (1975).
10. Asprey, L. B., and Matwiyoff, N. A., *Inorg. Nucl. Chem.—Herbert H. Hyman Mem. Vol.* p. 123 (1976).
11. Azeem, M., Brownstein, M., and Gillespie, R. J., *Can. J. Chem.* **47,** 4159 (1969).
12. Baird, H. W., and Giles, H. F., *Acta Crystallogr., Sect. A* **25,** 115 (1969).
13. Baran, E. J., *J. Fluorine Chem.* **10,** 255 (1977).
14. Barrow, R. F., Chandler, G. G., and Meyer, C. B., *Philos. Trans. R. Soc. London, Ser. A* **260,** 395 (1966).
15. Bartlett, N., Einstein, F., Stewart, D. F., and Trotter, J., *J. Chem. Soc. A* p. 1190 (1967).
16. Bartlett, N., and Robinson, P. L., *J. Chem. Soc.* p. 3417 (1961).
17. Berry, F. J., Kustan, E. H., Roshani, M., and Smith, B. C., *J. Organomet. Chem.* **99,** 115 (1975).
18. Birchall, T., Gillespie, R. J., and Vekris, S. L., *Can. J. Chem.* **43,** 1672 (1965).
19. Bladon, P., Brown, D. H., Crosbie, K. D., and Sharp, D. W. A., *Spectrochim. Acta, Part A* **26,** 2221 (1970).
20. Boate, A. R., Morton, J. R., and Preston, K. F., *J. Magn. Reson.* **29,** 243 (1978).
21. Bosworth, Y. M., Clark, R. J. H., and Rippon, D. M., *J. Mol. Spectrosc.* **46,** 240 (1973).
22. Bowater, I. C., Brown, R. D., and Burden, F. R., *J. Mol. Spectrosc.* **23,** 272 (1967).
23. Bowater, I. C., Brown, R. D., and Burden, F. R., *J. Mol. Spectrosc.* **28,** 454 (1968).
24. Brooks, W. V. F., Eshaque, M., Lau, C., and Passmore, J., *Can. J. Chem.* **54,** 817 (1976).
25. Brownstein, M., and Gillespie, R. J., *J. Chem. Soc. A* p. 67 (1973).

26. Bürger, H., *Z. Anorg. Allg. Chem.* **360,** 97 (1968).
27. Byström, A., and Wilhelmi, K. A., *Ark. Kemi* **3,** 461 (1951).
28. Carré, J., Claudy, P., Kollmannsberger, M., Bousquet, J., Garnier, E., and Barberi, P., *J. Fluorine Chem.* **11,** 613 (1978).
29. Carré, J., Claudy, P., Letoffe, J. M., Kollmannsberger, M., and Bousquet, J., *J. Fluorine Chem.* **14,** 139 (1979).
30. Carré, J., Germain, P., Kollmannsberger, M., Perachon, G., and Thourney, J., *J. Fluorine Chem.* **13,** 365 (1979).
31. Carrington, A., Currie, G. N., Miller, T. A., and Levy, D. H., *J. Chem. Phys.* **50,** 2726 (1969).
32. Cavanough, J. R., and Dailey, B. P., *J. Chem. Phys.* **34,** 1099 (1961).
33. Cernik, M., and Dostal, K., *Z. Anorg. Allg. Chem.* **425,** 37 (1976).
34. Chaigneau, M., and Santarromana, M., *C. R. Hebd. Seances Acad. Sci., Ser. C* **269,** 1643 (1969).
35. Christe, K. O., and Sawodny, W., *J. Chem. Phys.* **52,** 6320 (1970).
36. Christe, K. O., Schack, C. J., and Curtis, E. C., *Inorg. Chem.* **11,** 583 (1972).
37. Claasen, H. H., Goodman, G. L., Holloway, J. H., and Selig, H., *J. Chem. Phys.* **53,** 341 (1970).
38. Clark, R. J. H., and D'Urso, N. R., *J. Chem. Soc., Dalton Trans.* p. 170 (1978).
39. Clouston, A., Peacock, R. D., and Fraser, G. W., *Chem. Commun.* p. 1197 (1970).
40. Cohen, B., and Peacock, R. D., *Adv. Fluorine Chem.* **6,** 343 (1970).
41. Colton, S., Margrave, J. L., and Wilson, P. W., *Synth. Inorg. Met.-Org. Chem.* **1,** 149 (1971).
42. Compton, R. N., and Cooper, C. D., *J. Chem. Phys.* **59,** 4140 (1973).
43. Dailey, B. P., and Shoolery, J. N., *J. Am. Chem. Soc.* **77,** 3977 (1955).
44. Dalton, J., McFarlane, W., Wickens, C. R., Fraser, G. W., and Millar, J. B., *Org. Magn. Reson.* **8,** 522 (1976).
45. Derkasch, N. Ya., and Barashenkov, G. G., *Zh. Org. Khim.* **10,** 2619 (1974).
46. Desjardins, C. D., Lau, C., and Passmore, J., *Inorg. Nucl. Chem. Lett.* **10,** 151 (1974).
47. Dobud, P., and Jones, C. H. W., *J. Solid State Chem.* **16,** 201 (1976).
48. Dostal, K., *Inorg. Chem., Ser. Two* **3,** 85 (1975).
49. Dostal, K., and Cernik, M., *Z. Chem.* **6,** 424 (1966).
50. Edwards, A. J., *J. Chem. Soc.* p. 3714 (1964).
51. Edwards, A. J., and Jones, G. R., *J. Chem. Soc. A* p. 2858 (1968).
52. Edwards, A. J., and Jones, G. R., *J. Chem. Soc. A* p. 1491 (1970).
53. Edwards, A. J., and Jones, G. R., *J. Chem. Soc. A* p. 1891 (1970).
54. Edwards, A. J., and Hewaidy, F. I., *J. Chem. Soc. A* p. 2977 (1968).
55. Edwards, A. J., and Mouty, M. A., *J. Chem. Soc. A* p. 703 (1969).
56. Edwards, A. J., and Taylor, P., *J. Chem . Soc. A* p. 2150 (1973).
57. Elgad, U., and Selig, H., *Inorg. Chem.* **14,** 140 (1975).
58. Engelbrecht, A., Loreck, W., and Nehoda, W., *Z. Anorg. Allg. Chem.* **360,** 88 (1968).
59. Engelbrecht, A., and Sladky, F., *Angew. Chem.* **76,** 379 (1964); *Angew. Chem., Int. Ed. Engl.* **3,** 383 (1964).
60. Engelbrecht A., and Sladky, F., *Inorg. Nucl. Chem. Lett.* **1,** 15 (1965).
61. Engelbrecht, A., and Sladky, F., *Monatsh. Chem.* **96,** 159 (1965).
62. Engelbrecht, A., and Sladky, F., *Monatsh. Chem.* **96,** 360 (1965).
63. Engelbrecht, A., and Sladky, F., *Inorg. Chem., Ser. Two* **3.,** 137 (1975).
64. Engelbrecht, A., and Stoll, B., *Z. Anorg. Allg. Chem.* **292,** 20 (1957).
65. Evans, J. A., and Long, D. A., *J. Chem. Soc. A.,* p. 1688 (1968).

66. Ewing, V. C., and Sutton, L. E., *Trans. Faraday Soc.* **59,** 1241 (1963).
67. Fraser, G. W., and Meikle, G. D., *Chem. Commun.* p. 624 (1974).
68. Fraser, G. W., and Meikle, G. D., *J. Chem. Soc., Perkin Trans. 2* p. 312 (1975).
69. Fraser, G. W., and Meikle, G. D., *J. Chem. Soc., Dalton Trans.* p. 1033 (1975).
70. Fraser, G. W., and Meikle, G. D., *J. Chem. Soc., Dalton Trans.* p. 1985 (1977).
71. Fraser, G. W., and Millar, J. B., *Chem. Commun.* p. 1113 (1972).
72. Fraser, G. W., and Millar, J. B., *J. Chem. Soc., Dalton Trans.* p. 2029 (1974).
73. Fraser, G. W., Peacock, R. D., and McFarlane, W., *Mol. Phys.* **17,** 291 (1969).
74. Fraser, G. W., Peacock, R. D., and Watkins, P. M., *Chem. Commun.* p. 1248 (1967).
75. Fraser, G. W., Peacock, R. D., and Watkins, P. M., *Chem. Commun.* p. 1257 (1968).
76. Fraser, G. W., Peacock, R. D., and Watkins, P. M., *J. Chem. Soc. A* p. 1125 (1971).
77. Frey, R. A., Redington, R. L., and Aljibury, A. L. K., *J. Chem. Phys.* **54,** 344 (1971).
78. Furin, G., Terenteva, T. V., and Yakobson, G. G., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* p. 78 (1972).
79. Gibb, T. G., Greatex, R., Greenwood, N. N., and Sarma, A. C., *J. Chem. Soc. A* p. 212 (1970).
80. Gillespie, R. J., *J. Chem. Educ.* **40,** 295 (1963); "Molecular Geometry," Van Nostrand-Reinhold, Princeton, New Jersey, 1972.
81. Gillespie, R. J., and Whitla, W. A., *Can. J. Chem.* **47,** 4153 (1969).
82. Gillespie, R. J., and Whitla, W. A., *Can. J. Chem.* **48,** 657 (1970).
83. Gillespie, R. J., and Spekkens, P., *J. Fluorine Chem.* **7,** 43 (1976).
84. Greenwood, N. N., Sarma, A. C., and Straughan, P. B., *J. Chem. Soc. A* p. 1446 (1966).
85. Greenwood, N. N., Sarma, A. C., and Straughan, B. P., *J. Chem. Soc. A* p. 1561 (1968).
86. Gundersen, G., Hedberg, K., and Strand, T. G., *J. Chem. Phys.* **68,** 3548 (1978).
87. Haas, A., and Willner, H., *Spectrochim. Acta, Part A* **34,** 541 (1978).
88. Haas, A., and Willner, H., *Ber. Bunsenges. Phys. Chem.* **82,** 24 (1978); *Z. Anorg. Allg. Chem.* **454,** 17 (1979).
89. Hagen, A. P., and Elphingstone, E. A., *Inorg. Chem.* **12,** 478 (1973).
90. Hammond, P. R., *J. Chem. Soc. A* p. 3826 (1971).
91. Hammond, P. R., and Lake, R. R., *Chem. Commun.* p. 987 (1968).
92. Hammond, P. R., and Lake, R. R., *J. Chem. Soc. A* p. 3819 (1971).
93. Harland, P. W., and Thynne, J. C. J., *Inorg. Nucl. Chem. Lett.* **9,** 265 (1973).
94. Hermodsson, Y., *Acta Chem. Scand.* **21,** 1313 (1967).
95. Jones, G. R., Durbank, R. D., and Bartlett, N., *Inorg. Chem.* **9,** 2264 (1970).
96. Jumas, J. C., Maurin, M., and Philippot, E., *J. Fluorine Chem.* **8,** 329 (1976).
97. Jumas, J. C., Maurin, M., and Philippot, E., *J. Fluorine Chem.* **10,** 219 (1977).
98. Jumas, J. C., Vermot-Gaud-Daniel, and Philippot, E., *C. R. Hebd. Seances Acad. Sci.* 282 (1976).
99. Junkins, J. H., Bernhardt, H. A., and Barber, E. J., *J. Am. Chem. Soc.* **74,** 5749 (1952).
100. Kirchhoff, W. H., Johnson, D. R., and Powell, F. X., *J. Mol. Spectrosc.* **48,** 157 (1973).
101. Kolditz, L., and Fitz, I., *Z. Anorg. Allg. Chem.* **349,** 175 (1967).
102. Kolditz, L., and Fitz, I., *Z. Anorg. Allg. Chem.* **349,** 184 (1967).
103: Königer, F., Müller, A., and Selig, H., *Mol. Phys.* **34,** 1629 (1977).
104. Labonville, P., Ferraro, J. R., Wall, M. C., and Basile, L. J., *Coord. Chem. Rev.* **7,** 257 (1972).
105. Larkin, R. H., Stidham, H. D., and Wynne, K. J., *Spectrochim. Acta, Part A* **27,** 2261 (1971).

106. Lau, C., and Passmore, J., *Inorg. Chem.* **13,** 2278 (1974).

107. Lau, C., and Passmore, J., *J. Fluorine Chem.* **6,** 77, (1975).

108. Lau, C., and Passmore, J., *J. Fluorine Chem.* **7,** 261 (1976).

109. Legon, A. C., *J. Chem. Soc., Faraday Trans. 2* **69,** 29 (1973).

110. Lehmann, E., *J. Chem. Res. (S)* p. 42 (1978).

111. Lentz, D., Pritzkow, H., and Seppelt, K., *Angew. Chem.* **89,** 741 (1977); *Angew. Chem., Int. Ed. Engl.* 16, 729 (1977).

112. Lentz, D., Pritzkow, H., and Seppelt, K., *Inorg. Chem.* 17, 1926 (1978).

113. Lentz, D., and Seppelt, K., *Angew. Chem.* **90,** 390 (1978); *Angew. Chem., Int. Ed. Engl.* **90,** 355 (1978).

114. Lentz, D., and Seppelt, K., *Angew. Chem.* **90,** 391 (1978); *Angew. Chem., Int. Ed. Engl.* **90,** 356 (1978).

115. Lentz, D., and Seppelt, K., *Angew. Chem.* **91,** 68 (1979); *Angew. Chem., Int. Ed. Engl.* **91,** 66 (1979).

116. Levin, I. W., and Berney, C. V., *J. Chem. Phys.* **44,** 2557 (1966).

117. Mastin, S. H., Ryan, R. R., and Asprey, L. B., *Inorg. Chem.* **9,** 2101 (1970).

118. Mayer, E., and Sladky, F., *Inorg. Chem.* **14,** 589 (1975).

119. Milne, J. B., and Mofett, D., *Inorg. Chem.* **12,** 2240 (1973).

120. Mitra, G., and Cady, G. H., *J. Am. Chem. Soc.* **81,** 1646 (1959).

121. Morris, R. J., and Moss, K. C., *J. Fluorine Chem.* **13,** 551 (1979).

122. Morton, J. R., Preston, K. F., and Tait, J. C., *J. Chem. Phys.* **62,** 2029 (1975).

123. Moss, J. H., Ottie, R., and Wilford, J. B., *J. Fluorine Chem.* **3,** 317 (1973–1974).

124. Muetterties, E. L., and Phillips, W. D., *J. Am. Chem. Soc.* **81,** 1084 (1959).

125. Müller, A., Fadini, A., and Peacock, C., *Z. Phys. Chem. (Leipzig)* **238,** 17 (1968).

126. Oberhammer, H., and Seppelt, K., *Angew. Chem.* **90,** 66 (1978); *Angew. Chem., Int. Ed. Engl.* **17,** 69 (1978).

127. Oberhammer, H., and Seppelt, K., *Inorg. Chem.* **17,** 1435 (1978).

128. Oberhammer, H., and Seppelt, K., *Inorg. Chem.* **18,** 2226 (1979).

129. Olah, G. A., Nojima M. and Kerekes, I., *J. Am. Chem. Soc.* **96,** 925 (1974).

130. Paetzold, R., and Aurich, K., *Z. Anorg. Allg. Chem.* **335,** 281 (1965).

131. Paetzold, R., and Aurich, K., *Z. Anorg. Allg. Chem.* **348,** 94 (1966).

132. Paetzold, R., Kurze, R., and Engelhard, G., *Z. Anorg. Allg. Chem.* **352,** 62 (1967).

133. Peacock, R. D., *J. Chem. Soc.* p. 3617 (1953).

134. Pitts, J. J., and Jache, A. W., *Inorg. Chem.* **7,** 1661 (1968).

135. Porcham, W., and Engelbrecht, A., *Z. Phys. Chem. (Leipzig)* **248,** 177 (1971).

136. Porcham. W., and Engelbrecht, A., *Monatsh. Chem.* **102,** 333 (1971).

137. Pritzkow, H., and Seppelt, K., *Angew. Chem.* **88,** 846 (1976); *Angew. Chem., Int. Ed. Engl.* **15,** 771 (1976).

138. Pritzkow, H., and Seppelt, K., *Inorg. Chem.* **16,** 2685 (1977).

139. Ramaswamy, K., and Mohan, N., *J. Mol. Struct.* **7,** 51, (1971).

140. Reichenbaecher, M., and Paetzold, R., *Z. Anorg. Allg. Chem.* **400,** 176 (1973).

141. Reichert, W. L., and Cady, G. H., *Inorg. Chem.* **12,** 769 (1973).

142. Rode, B. M., Engelbrecht, A., and Schantl, J., *Z. Phys. Chem. (Leipzig)* **253,** 17 (1973).

143. Ruzicka, A., *Z. Chem.* **19,** 75 (1979).

144. Schack, C. J., Wilson, R. D., and Hon, J. F., *Inorg. Chem.* **11,** 208 (1972).

145. Seel, F., and Golitz, D., *Z. Anorg. Allg. Chem.* **327,** 28 (1964).

146. Seel, F., and Gombler, W., *J. Fluorine Chem.* **4,** 327 (1974).

147. Selected Values of Chemical Thermodynamics Properties, *Natl. Bur. Stand. (U.S.), Circ.* **500** (1961).

148. Selig, H., Sarig, S., and Abramowitz, S., *Inorg. Chem.* **13,** 1508 (1974).

149. Seppelt, K., *Angew. Chem.* **84,** 212 (1972); *Angew. Chem., Int. Ed. Engl.* 11, 723 (1972).
150. Seppelt, K., *Angew. Chem.* **84,** 715 (1972); *Angew. Chem., Ed. Engl.* **84,** 723 (1972).
151. Seppelt, K., *Chem. Ber.* **105,** 2431 (1972).
152. Seppelt, K., *Chem. Ber.* **105,** 3131 (1972).
153. Seppelt, K., *Chem. Ber.* **106,** 157 (1973).
154. Seppelt, K., *Chem. Ber.* **106,** 1920 (1973).
155. Seppelt, K., *Inorg. Chem.* **12,** 2837 (1973).
156. Seppelt, K., *Z. Anorg. Allg. Chem.* **399,** 65 (1973).
157. Seppelt, K., *Z. Anorg. Allg. Chem.* **399,** 87 (1973).
158. Seppelt, K., *Angew. Chem.* **86,** 103 (1974); *Angew. Chem., Int. Ed. Engl.* **13,** 91 (1974).
159. Seppelt, K., *Angew. Chem.* **86,** 104 (1974); *Angew. Chem., Ed. Engl.* **13,** 92 (1974).
160. Seppelt, K., *Z. Anorg. Allg. Chem.* **406,** 287 (1974).
161. Seppelt, K., *Z. Anorg. Allg. Chem.* **416,** 12 (1975).
162. Seppelt, K., *Chem. Ber.* **108,** 1823 (1975).
163. Seppelt, K., *Chem. Ber.* **109,** 1046 (1976).
164. Seppelt, K., *Chem. Ber.* **110,** 1470 (1977).
165. Seppelt, K., and Nothe, D., *Inorg. Chem.* **12,** 2727 (1973).
166. Shpinel, V. S., Brynkhanov, V. A., Kothekar, V., Iofa, B. Z., and Semenov, S. I., *Symp. Faraday Soc.* **1,** 69 (1968).
167. Siebert, H., "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie." Springer-Verlag, Berlin and New York 1966.
168. Sladky, F., *Angew. Chem.* **81,** 330 (1969); *Angew. Chem., Int. Ed. Engl.* **8,** 373 (1969).
169. Sladky, F., *Angew. Chem.* **81,** 536 (1969); *Angew. Chem., Int. Ed. Engl.* **8,** 523 (1969).
170. Sladky, F., *Angew. Chem.* **82,** 357 (1970); *Angew. Chem., Int. Ed. Engl.* **82,** 375 (1970).
171. Sladky, F., *Monatsh. Chem.* **101,** 1559 (1970).
172. Sladky, F., *Monatsh. Chem.* **101,** 1571 (1970).
173. Sladky, F., *Monatsh. Chem.* **101,** 1577 (1970).
174. Sladky, F., and Kropshofer, K., *Inorg. Chem. Lett.* **8,** 195 (1972).
175. Sladky, F., and Kropshofer, H., *Chem. Commun.* p. 600 (1973).
176. Sladky, F., and Kropshofer, H., to be published.
177. Sladky, F., Kropshofer, H., and Leitzke, O., *Chem. Commun.* p. 134 (1973).
178. Sladky, F., Kropshofer, H., Leitzke, O., and Peringer, P., *J. Inorg. Nucl. Chem.—Herbert H. Hyman Mem. Vol.* p. 69 (1976).
179. Sladky, F., and Leitzke, O., *Z. Anorg. Allg. Chem.* (in press).
180. Sladky, F., and Schröder, K., *Z. Anorg. Allg. Chem.* (in press).
181. Sladky, F., and Schröder, K., *Chem. Ber.* **113,** 1414 (1980).
182. Smith, J. E., and Cady, G. H., *Inorg. Chem.* **9,** 1293 (1970).
183. So, S. P., Li K. K., and Hung. L. K., *Bull. Soc. Chim. Belg.* **87,** 411 (1978).
184. Stockdale, J. A. D., Compton, R. N., and Schweinler, H. C., *J. Chem. Phys.* **53,** 1502 (1970).
185. Takeo, H., Hirota, E., and Morino, Y., *J. Mol. Spectrosc.* **34,** 370 (1970).
186. Templeton, L. K., Templeton, D. H., Bartlett, N., and Seppelt, K., *Inorg. Chem.* **15,** 2720 (1976).
187. Templeton, L. K., Templeton, D. H., Seppelt, K., and Bartlett, N. *Inorg. Chem.* **15,** 2718 (1976).

188. Tolles, W. M., and Gwinn, W. D., *J. Chem. Phys.* **36,** 1119 (1962).
189. Touzin, J., Meznik, L., and Mitacek, L., *Collect. Czech. Chem. Commun.* **44,** 1530 (1979).
190. Vasile, M. J., Stevie, F. A., and Seppelt, K., *J. Fluorine Chem.* **13,** 487 (1979).
191. Watkins, P. M., *J. Chem. Educ.* **51,** 520 (1974).
192. Wynne, K. J., *Inorg. Chem.* **9,** 299 (1970).
193. Wynne, K. J., *Inorg. Chem.* **10,** 1868 (1971).