

to that observed²⁷ for $\text{ClO}_2 + \text{AsF}_6^-$. The latter has a tetragonal unit cell with $a = 10.39$ and $c = 8.03$ Å. The unit cell of $\text{ClF}_2\text{O} + \text{PtF}_6^-$ might be derived from the $\text{ClO}_2 + \text{AsF}_6^-$ cell by assuming orthorhombic distortion due to the lower symmetry of the ClF_2O^+ cation. Further evidence for the formulation of the solid as ClF_2O^+

(27) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, **8**, 2489 (1969).

PtF_6^- can be deduced from the fact that the X-ray powder diffraction patterns of $\text{ClF}_2\text{O} + \text{AsF}_6^-$ and $\text{ClF}_2\text{O} + \text{PtF}_6^-$ are almost identical.

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Chlorine Trifluoride Oxide. V. Complex Formation with Lewis Acids and Bases

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Chlorine trifluoride oxide, ClF_3O , exhibits amphoteric character. With the strong Lewis bases CsF , RbF , and KF it forms the stable, white, crystalline adducts, $\text{CsF} \cdot \text{ClF}_3\text{O}$, $\text{RbF} \cdot \text{ClF}_3\text{O}$, and $\text{KF} \cdot \text{ClF}_3\text{O}$, respectively. With the weaker base FNO it neither forms a complex nor chemically interacts at temperatures as low as -95° . With the Lewis acids SbF_5 , AsF_5 , and BF_3 it forms white, crystalline 1:1 adducts, whereas with SiF_4 it forms a 2:1 adduct. The thermal stability of these adducts decreases in the order: $\text{ClF}_3\text{O} \cdot \text{SbF}_5 > \text{ClF}_3\text{O} \cdot \text{AsF}_5 > \text{ClF}_3\text{O} \cdot \text{BF}_3 > (\text{ClF}_3\text{O})_2 \cdot \text{SiF}_4$. The dissociation pressure-temperature relation has been measured and thermodynamic data are calculated for the process $(\text{ClF}_3\text{O})_2 \cdot \text{SiF}_4(\text{s}) \rightleftharpoons 2\text{ClF}_3\text{O}(\text{g}) + \text{SiF}_4(\text{g})$. The tendencies of adduct formation are compared for ClF_3O , ClF_5 , ClO_2F , ClF_3 , and ClF and are correlated with the structural stability of the halogen fluorides and their corresponding ions.

Introduction

Halogen fluorides and oxyfluorides generally exhibit amphoteric character.¹ Consequently, we considered that ClF_3O might also form complexes with strong Lewis acids and bases. In this paper we report on the syntheses and some of the properties of a number of adducts derived from ClF_3O .

Experimental Section

Materials and Apparatus.—Experimental techniques used in these studies were essentially the same as those described elsewhere.²⁻⁶ The preparation and purification of ClF_3O and FNO are described elsewhere.^{2,7} The alkali metal fluorides were fused in a platinum crucible and powdered in a drybox prior to use. Arsenic pentafluoride (from Ozark Mahoning Co.), BF_3 , and SiF_4 (both from the Matheson Co.) were purified by fractional condensation. Antimony pentafluoride (from Ozark Mahoning Co.) was purified by vacuum distillation at ambient temperature. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra.

Preparation of Alkali Metal Fluoride- ClF_3O Adducts.—Dry CsF (66.0 mmol) was placed into a 90-ml prepassivated Monel cylinder, and purified ClF_3O (106.4 mmol) was added at -196° . The cylinder was kept at ambient temperature for 30 days. Unreacted ClF_3O (40.5 mmol) was removed *in vacuo* and identified by its infrared spectrum. The cylinder was opened in the glove box and contained 17.1 g of a stable, white, crystalline solid (weight calculated for $\text{Cs}^+\text{ClF}_4\text{O}^-$, 17.18 g). Therefore, CsF (66.0 mmol) had reacted with ClF_3O (65.9 mmol) in a mole ratio of 1:0.998 producing the complex $\text{Cs}^+\text{ClF}_4\text{O}^-$.

Similarly, RbF (92.0 mmol), when combined with ClF_3O (93.5 mmol) at -196° and shaken at ambient temperature for 2 days,

reacted with ClF_3O (67.15 mmol) producing the complex $\text{Rb}^+\text{ClF}_4\text{O}^- \cdot 0.28\text{RbF}$.

Pure ClF_3O (purity 99+%) was loaded into a 316 stainless steel cylinder containing a large excess of dry KF . After the contents of the cylinder was kept at ambient temperature for 30 days, practically all of the ClF_3O had complexed with KF .

The $\text{FNO}-\text{ClF}_3\text{O}$ System.—Nitrosyl fluoride (25.6 mmol) and ClF_3O (12.8 mmol) were combined at -196° in a Teflon FEP U trap. The mixture was allowed to warm to -79° and was kept at this temperature for 24 hr. It remained at all times a water-clear liquid and no sign of solid formation could be observed. The vapor pressure above the liquid was about 115 mm. The contents of the trap was cooled to -95° , and FNO (25.5 mmol) was removed by vacuum distillation. The residue (12.7 mmol) was shown by its infrared spectrum to be essentially pure ClF_3O . Hence, ClF_3O and FNO do not form a stable complex at -95° .

Preparation of ClF_3O -Lewis Acid Adducts.—Boron trifluoride (4.00 mmol) and ClF_3O (3.22 mmol) were combined at -196° in a Teflon FEP container. The mixture was allowed to warm up slowly to ambient temperature and was kept at this temperature for 12 hr. Unreacted BF_3 (0.74 mmol) was removed *in vacuo* at 20° and identified by its infrared spectrum. The white, crystalline residue had no detectable dissociation pressure at 20° . Therefore, ClF_3O (3.22 mmol) had reacted with BF_3 (3.26 mmol) in a mole ratio of 1:1.01, producing the complex $\text{ClF}_3\text{O} \cdot \text{BF}_3$.

Similarly, AsF_5 (16.4 mmol) and ClF_3O (13.2 mmol) were combined at -196° . After keeping the mixture at 20° for 2 hr, unreacted AsF_5 (2.8 mmol) was removed *in vacuo* at 20° . Therefore, ClF_3O (13.2 mmol) had reacted with AsF_5 (13.6 mmol) in a mole ratio of 1:1.03 producing the white, crystalline, stable complex, $\text{ClF}_3\text{O} \cdot \text{AsF}_5$.

Silicon tetrafluoride (3.79 mmol) was combined with ClF_3O (5.02 mmol) at -196° . When the mixture was allowed to warm up to about -80° , complex formation occurred. Unreacted SiF_4 (1.21 mmol) was removed *in vacuo* at -64° and identified by its infrared spectrum. Therefore, ClF_3O (5.02 mmol) had reacted with SiF_4 (2.58 mmol) in a mole ratio of 2:1.03, producing the white, crystalline complex $(\text{ClF}_3\text{O})_2 \cdot \text{SiF}_4$.

Antimony pentafluoride (104 mmol) and ClF_3O (20.9 mmol) were combined in a 150-ml prepassivated Monel cylinder at -196° . The contents of the cylinder was kept in an electrically heated oven at 135° for 6 days under autogenous pressure. Unreacted SbF_5 was removed by vacuum distillation at 130° .

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(2) D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, *Inorg. Chem.*, **11**, 2189 (1972).

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(4) K. O. Christe and E. C. Curtis, *ibid.*, **11**, 2196 (1972).

(5) C. J. Schack, C. B. Lindahl, D. Pilipovich, and K. O. Christe, *ibid.*, **11**, 2201 (1972).

(6) D. Pilipovich, R. D. Wilson, and H. F. Bauer, U. S. Patent, to be issued, 1972.

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The cylinder was opened in the glove box and contained 7.8 g of a white, crystalline solid (calculated weight for 20.9 mmol of $\text{ClF}_3\text{O}\cdot\text{SbF}_5$, 6.8 g; for 20.9 mmol of $\text{ClF}_3\text{O}\cdot 2\text{SbF}_5$, 11.3 g). Therefore, ClF_3O had reacted with SbF_5 in a mole ratio of 1:1.22.

Dissociation Pressure Measurements.—The $(\text{ClF}_3\text{O})_2\cdot\text{SiF}_4$ complex was prepared in a Teflon FEP container directly connected to a Heise, Bourdon-tube-type gauge (0–1500 mm \pm 0.1%). The temperature of the cooling bath was determined with a copper-constantan thermocouple. To be certain that an equilibrium existed at each temperature reading, a sample of the gas above the solid complex was pumped off and a constant pressure was reestablished. True equilibrium existed at a given temperature if the pressures, before and after the pumping off procedure, were identical. Equilibrium pressures were always approached from below a given temperature. The following temperature ($^\circ\text{C}$)–vapor pressure (mm) relation was observed: –30.9, 4; –24.5, 8; 0.0, 72; 6.0, 124; 15.7, 257; and 20.8, 380. The best fit of $\log P$ vs. T^{-1} (in $^\circ\text{K}$) was obtained by the method of least squares.

X-Ray Powder Data.—Debye–Scherrer powder patterns were taken as previously described.⁵

Results and Discussion

Synthesis.—Chlorine trifluoride oxide and the alkali metal fluorides, CsF , RbF , and KF , when combined at ambient temperature, produced the 1:1 complexes, $\text{CsF}\cdot\text{ClF}_3\text{O}$, $\text{RbF}\cdot\text{ClF}_3\text{O}$, and $\text{KF}\cdot\text{ClF}_3\text{O}$, respectively. For CsF a practically quantitative conversion to $\text{CsF}\cdot\text{ClF}_3\text{O}$ was achieved, whereas for RbF the conversion to $\text{RbF}\cdot\text{ClF}_3\text{O}$ was only 78%. In the case of RbF , however, a considerably shorter reaction time and a nearly stoichiometric amount of starting materials were employed in the synthesis. Hence, the conversion of RbF to $\text{RbF}\cdot\text{ClF}_3\text{O}$ could almost certainly be increased by using an excess of ClF_3O , a longer reaction time, and a slightly increased reaction temperature. The fact that a high conversion to the corresponding alkali metal salt becomes increasingly difficult with decreasing atomic weight of the alkali metal has also been observed in the case of the ClF_2^- and ClF_4^- salts.^{8,9} This might be due to various effects such as changes in lattice energy, solubility in the excess halogen fluoride or oxyfluoride, and stability of the adducts.

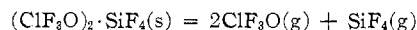
No indication for the formation of a stable complex between FNO and ClF_3O was found at temperatures as low as -95° . The fact that only a liquid phase was observed at relatively low temperatures where pure ClF_3O (mp, -42°) is a solid indicates high miscibility or solubility of ClF_3O in FNO. The vapor pressure of ~ 115 mm observed at -78.8° above the liquid phase is only slightly lower than the value of 137 mm calculated for an ideal 1:2 mixture from Raoult's law.

Chlorine trifluoride oxide forms stable 1:1 adducts with the Lewis acids AsF_5 and BF_3 . In spite of the excess Lewis acid employed in the syntheses, no evidence for the formation of di- or polymeric anions, such as $\text{B}_2\text{F}_7^{10-12}$ or $\text{As}_2\text{F}_{11}^{12,13}$ was obtained. However, in the case of SbF_5 , a product having the composition (according to its infrared spectrum and the material balance) of $\text{ClF}_2\text{O}^+\text{SbF}_6^- \cdot 0.28\text{ClF}_2\text{O}^+\text{Sb}_2\text{F}_{11}^-$ was obtained. The formation of some $\text{Sb}_2\text{F}_{11}^-$ salt^{14–16} is not

surprising since a large excess of SbF_5 was used in the synthesis. No attempts were made to optimize the reaction conditions for the synthesis of $\text{ClF}_2\text{O}^+\text{SbF}_6^-$. However, using a large excess of ClF_3O , decreasing the reaction temperature, and adding the SbF_5 (preferably in a solvent such as HF^{12}) slowly to the excess ClF_3O should result in a better defined 1:1 adduct.

The difunctional Lewis acid SiF_4 , when combined with ClF_3O at about -80° , forms the expected 1:2 complex. The lower temperature required for the synthesis of $(\text{ClF}_3\text{O})_2\cdot\text{SiF}_4$ is due to the decreased thermal stability of the adduct.

Properties.—The 1:1 adducts of ClF_3O with SbF_5 , AsF_5 , and BF_3 are white, crystalline solids showing no measurable dissociation pressure at ambient temperature. The thermal stability of the Lewis acid adducts decreases in the order $\text{ClF}_3\text{O}\cdot\text{SbF}_5 > \text{ClF}_3\text{O}\cdot\text{AsF}_5 > \text{ClF}_3\text{O}\cdot\text{BF}_3 > (\text{ClF}_3\text{O})_2\cdot\text{SiF}_4$. Thus, $\text{ClF}_3\text{O}\cdot\text{SbF}_5$ is stable at 130° *in vacuo*, whereas $(\text{ClF}_3\text{O})_2\cdot\text{SiF}_4$ reaches a dissociation pressure of 760 mm at 31° . Based on the observed dissociation pressure–temperature data, a plot of $\log P_{\text{mm}}$ vs. T^{-1} (in $^\circ\text{K}$) for the heterogeneous equilibrium



is a straight line. The equation $\log P_{\text{mm}} = 11.8018 - 2712.3/T$ represents these data in the temperature range -30.9 to 20.8° . The standard error of the estimate of $\log P$ was 0.008 which corresponds to 2% deviation in pressure. The index of correlation (ρ) is 0.999938.

By extrapolation, a dissociation pressure of 1 atm was obtained at 30.9° . At 25° the dissociation pressure amounts to 408 mm. From the slope of the $\log P_{\text{mm}}$ vs. T^{-1} curve, $\Delta H_d^\circ = 37.24$ kcal mol⁻¹ was found.¹⁷ From $\Delta F^\circ_T = -RT \ln K_{p_{\text{atm}}}$, a free energy change, $\Delta F^\circ_{298} = 1.846$ kcal mol⁻¹, and from $\Delta S^\circ_T = (\Delta H^\circ - \Delta F^\circ_T)T^{-1}$, an entropy change, $\Delta S^\circ_{298} = 118.7$ cal deg⁻¹ mol⁻¹, were found for the dissociation process at 25° . A heat of formation of $(\text{ClF}_3\text{O})_2\cdot\text{SiF}_4(\text{s})$, $\Delta H_f^\circ_{298} = 488.4 \pm 6$ kcal mol⁻¹, was calculated based upon $\Delta H_f^\circ_{298}[\text{SiF}_4(\text{g})]^{18} = 385.980$ kcal mol⁻¹ and $\Delta H_f^\circ_{298}[\text{ClF}_3\text{O}(\text{g})]^{19} = -32.6 \pm 3$ kcal mol⁻¹. The uncertainty in the heat of formation value is mainly due to the uncertainty in the value of the heat of formation of aqueous HF^{20} used for calculating $\Delta H_f^\circ_{298}$ of ClF_3O . The heat of dissociation,¹⁷ 37.24 kcal mol⁻¹, obtained for $(\text{ClF}_2\text{O}^+)_2\text{SiF}_6^{2-}$ is of the same order of magnitude as the value obtained for the similar ionic 2:1 adduct $\text{FCl}_2^+\text{AsF}_6^-$ (32.8 kcal mol⁻¹).²¹

The Lewis base adducts $\text{Cs}^+\text{ClF}_4\text{O}^-$, $\text{Rb}^+\text{ClF}_4\text{O}^-$, and $\text{K}^+\text{ClF}_4\text{O}^-$ show no measurable dissociation pressure at ambient temperature. However, the least stable of these adducts *i.e.*, $\text{K}^+\text{ClF}_4\text{O}^-$, can be slowly dissociated *in vacuo* at ambient temperature. The increasing stability of the salts with increasing size of the

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(17) It is not strictly correct to infer that the measured heat of reaction for the dissociation process equals the thermodynamic heat of dissociation. This would only be appropriate if the complex were in the gas phase or if the heat of sublimation of the complex were zero. However, for convenience, ΔH_d° will be used throughout the text to mean the heat of reaction of a complete dissociation process of the type complex(s) = gas + gas.

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alkali metal cation is similar to that found for the corresponding ClF_2^- and ClF_4^- salts.^{8,9}

All of the described ClF_3O adducts are hygroscopic solids. They react violently with water and organic materials. The stable materials were stored in closed Teflon FEP containers at ambient temperature for several years without any signs of decomposition.

Structure of the Adducts.—X-Ray powder diffraction patterns were obtained for $\text{ClF}_2\text{O}+\text{AsF}_6^-$, $\text{ClF}_2\text{O}+\text{BF}_4^-$, and $\text{Cs}+\text{ClF}_4\text{O}^-$. Table I lists the calculated and

$\text{ClO}_2+\text{AsF}_6^-$ ²² and $\text{ClF}_2\text{O}+\text{PtF}_6^-$ ⁵ one can deduce six molecules per unit cell for $\text{ClF}_2\text{O}+\text{AsF}_6^-$. This results in a reasonable^{23,24} value of 16.2 Å³ for the average volume per F or O atom neglecting contributions from the highly charged central atoms. For $\text{ClF}_2\text{O}+\text{BF}_4^-$ the unit cell dimensions are $a = 13.21$, $b = 13.62$, and $c = 9.63$ Å. These unit cell dimensions compare favorably with those of orthorhombic $\text{Cs}+\text{BF}_4^-$ ($a = 5.83$, $b = 7.65$, and $c = 9.43$ Å),²⁵ assuming the $\text{ClF}_2\text{O}+\text{BF}_4^-$ unit cell to be four times larger than that of $\text{Cs}+\text{BF}_4^-$. Therefore, the unit cell of $\text{ClF}_2\text{O}+\text{BF}_4^-$ should contain 16 molecules resulting in a plausible^{23,24} value of 15.5 Å³ for the average volume per F or O atom. The diffraction pattern of $\text{Cs}+\text{ClF}_4\text{O}^-$ was rather faint and contained too many lines to allow its indexing.

The vibrational spectra were recorded for $\text{Rb}+\text{ClF}_4\text{O}^-$, $\text{Cs}+\text{ClF}_4\text{O}^-$, $\text{ClF}_2\text{O}+\text{BF}_4^-$, $\text{ClF}_2\text{O}+\text{AsF}_6^-$, and $\text{ClF}_2\text{O}+\text{SbF}_6^-$ and are entirely consistent with ionic structures. A detailed discussion of the spectra and their assignment together with force constant calculations and bond-order considerations are published in separate papers.^{26,27}

General Considerations.—In the past the self-ionization of halogen fluorides has been overemphasized.¹ This was mainly due to the ease with which most of the reaction chemistry of the amphoteric halogen fluorides could be explained by it. However, except for BrF_3 , little or no evidence has been found supporting this postulated self-ionization. Furthermore, no attempts have been made to rationalize and correlate the available data on the tendency of various halogen fluorides to form adducts with Lewis acids or bases. Since reliable data are now available on the complex formation of pentavalent ClF_5 ,¹⁶ ClF_3O , and ClO_2F ,^{28,29} of trivalent ClF_3 ,^{9,30-36} and of monovalent ClF ,^{8,21,37,38} a meaningful comparison can be made.

A priori, the following trends might be expected within this series. (i) Compounds showing a strong tendency to form stable adducts with Lewis acids (and, hence, having considerable base character) should show a decreased tendency to form adducts with Lewis bases, and *vice versa*. (ii) The fluoride donor (*i.e.*, Lewis base) properties of a halogen fluoride should increase with increasing electron density on the fluoride ligands. Consequently, replacement of two fluorine ligands by one less electronegative oxygen ligand without changing the oxidation state of the central

TABLE I

X-RAY POWDER DATA FOR $\text{ClF}_2\text{O}+\text{AsF}_6^-$ AND $\text{ClF}_2\text{O}+\text{BF}_4^-$

$\text{ClF}_2\text{O}+\text{AsF}_6^-$				$\text{ClF}_2\text{O}+\text{BF}_4^-$			
$d, \text{Å}$			hkl	$d, \text{Å}$			hkl
Obsd	Calcd	Intens		Obsd	Calcd	Intens	
7.42	7.41	m	110	6.63	6.63	ms	200
5.47	5.46	m	111	4.82	4.82	m	002
4.98	4.97	mw	200	4.53	4.53	w	102
4.73	4.73	w	120	4.29	4.29	s	130
4.48	4.50	w	021	4.09	4.10	s	031
4.25	4.25	vs	201	3.75	3.74	w	230
4.09	4.09	s	121, 002	3.64	3.69	w	320
3.77	3.77	vw	102	3.40	3.40	vs	040
3.67	3.66	s	220	3.31	3.31	m	400
3.56	3.56	vw	112	3.03	3.03	w	240
3.37	3.37	vw	130	2.87	2.88	w	241
3.30	3.30	s	300, 031	2.81	2.82	w	213
3.15	3.15	w	202	2.67	2.67	m	150
2.96	2.96	m	311	2.61	2.62	w	051
2.92	2.92	w	230	2.59	2.59	w	510
2.73	2.73	mw	003, 222	2.56	2.57	w	151
2.60	2.60	vw	140	2.44	2.44	mw	251
2.55	2.55	w	113	2.33	2.33	m	114
2.49	2.49	w	400	2.20	2.20	m	600
2.34	2.34	vw	331	2.15	2.15	m	601
2.18	2.18	mw	421	2.06	2.06	w	343
2.14	2.14	mw	402	2.04	2.04	vw	621
2.08	2.08	vw	412	1.922	1.926	mw	170
2.02	2.02	mw	341	1.894		mw	
1.957	1.957	w	510, 323	1.840		w	
1.913	1.907	m	052	1.791		w	
1.883	1.885	w	143	1.759		w	
1.838	1.834	mw	403	1.714		vw	
1.762	1.764	vw	512	1.694		mw	
1.717	1.718	vw	314	1.572		w	
1.649		vw		1.544		vw	
1.594		m		1.520		vw	
1.585		w		1.503		w	
1.531		w		1.467		w	
1.486		w		1.446		w	
1.433		vw		1.410		mw	
1.418		vw		1.337		w	
1.387		w		1.314		w	
1.377		w		1.286		w	
1.358		vw		1.267		w	
1.334		vw		1.228		w	
1.318		w		1.131		w	
1.301		vw		1.106		w	
1.285		vw		1.079		w	
1.260		w		1.065		w	
1.241		w					
1.216		vw					
1.194		vw					
1.177		vw					

observed spacings for $\text{ClF}_2\text{O}+\text{AsF}_6^-$ and $\text{ClF}_2\text{O}+\text{BF}_4^-$. The patterns of both compounds were tentatively indexed in the orthorhombic system. The unit cell dimensions calculated for these data for $\text{ClF}_2\text{O}+\text{AsF}_6^-$ are $a = 9.94$, $b = 10.78$, and $c = 8.16$ Å. These values are very similar to those obtained for $\text{ClF}_2\text{O}+\text{PtF}_6^-$ ($a = 9.94$, $b = 11.12$, and $c = 8.21$ Å).⁵ By analogy with

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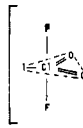
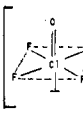
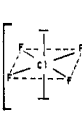
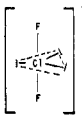











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ANION FORMED BY REACTION WITH LEWIS BASE INCREASING STRENGTH OF LEWIS BASE ↑	CsF	Cs ⁺ ClF ₂ O ₂ ^{-c}	[	Cs ⁺ ClF ₄ O ^{-d}	[	NO COMPLEX ^e	Cs ⁺ ClF ₆ ^{-g}	[	Cs ⁺ ClF ₂ ⁻ⁱ	[	
	RbF	NO COMPLEX ^b		Rb ⁺ ClF ₄ O ^{-d}		NO COMPLEX ^e	Rb ⁺ ClF ₆ ^{-g}		Rb ⁺ ClF ₂ ⁻ⁱ		
	KF	NO COMPLEX ^b		K ⁺ ClF ₄ O ^{-d}		NO COMPLEX ^e	K ⁺ ClF ₆ ^{-g}		K ⁺ ClF ₂ ⁻ⁱ		
	NOF	NO COMPLEX ^b		NO COMPLEX ^d		NO COMPLEX ^e	NO ⁺ ClF ₄ ^{-h} -50°		NO ⁺ ClF ₂ ⁻ⁱ -23°		
AMPHOTERIC PARENT MOLECULE (OXIDATION STATE OF CENTRAL ATOM)		ClO ₂ F (+IV)	[	ClF ₃ O (+IV)	[	ClF ₅ (+IV)	[	ClF ₃ (+III)	[	ClF (+I)	[
CATION FORMED BY REACTION WITH LEWIS ACID INCREASING STRENGTH OF LEWIS ACID ↓	SiF ₄		[	[ClF ₂ O ⁺ ·2SiF ₆ ^{-d}] 310°	[	NO COMPLEX ^e	[	[	[	[	
	BF ₃	ClO ₂ ⁺ BF ₄ ^{-c} -44°		ClF ₂ O ⁺ BF ₄ ^{-d}			ClF ₄ ⁺ AsF ₆ ^{-e} 23°		ClF ₂ ⁺ AsF ₆ ^{-h}		
	AsF ₅	ClO ₂ ⁺ AsF ₆ ^{-c}		ClF ₂ O ⁺ AsF ₆ ^{-d}			ClF ₄ ⁺ AsF ₆ ^{-e}		ClF ₂ ⁺ AsF ₆ ^{-h}		
	SbF ₅	ClO ₂ ⁺ SbF ₆ ^{-c}		ClF ₂ O ⁺ SbF ₆ ^{-d}			ClF ₄ ⁺ SbF ₆ ^{-e}		ClF ₂ ⁺ SbF ₆ ^{-h}		

a. REFERENCE 28 AND 29

b. REFERENCE 39

c. REFERENCE 22

d. THIS WORK AND REFERENCES 26 AND 27

e. REFERENCE 16

f. K. O. CHRISTE AND W. SAWADNY, TO BE PUBLISHED

g. REFERENCES 9, 35 AND 36

h. REFERENCES 30-34

i. REFERENCES 8, 37 AND 38

j. REFERENCE 21 AND R. J. GILLESPIE AND

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Figure 1.—Relative acid–base strength of various amphoteric halogen fluorides derived from their tendency to form adducts with strong Lewis acids and bases. Compounds of marginal stability are in larger type with the numbers indicating the temperature (°C) at which the dissociation pressure above the solid equals 760 mm.

atom (*i.e.*, $\text{ClF}_5 \rightarrow \text{ClF}_3\text{O} \rightarrow \text{ClFO}_2$) or replacement of two fluorine ligands by one free electron pair with change of the oxidation state of the central atom (*i.e.*, $\text{ClF}_5 \rightarrow \text{ClF}_3 \rightarrow \text{ClF}$) should increase the basicity of a halogen fluoride molecule. Hence, one would expect ClF_5 to have more acid character than either ClO_2F or ClF . Furthermore, one would expect these trends to be continuous.

Figure 1 shows the observed data. The size of the arrows indicates the tendency to form adducts. As can be seen both predictions made *a priori* cannot be the dominating factors. There is no continuous trend from ClF_5 toward either ClO_2F or ClF . Furthermore, ClF_3O and ClF_3 show a pronounced tendency to form adducts with both Lewis acids and Lewis bases. Consequently, the tendency to form adducts cannot depend strongly on the acid strength of the parent molecule. However, there seems to be a correlation between the tendency to form adducts and the structures of the parent molecule and the resulting ions. If, for example, the structure of the parent molecule is derived from the energetically less favorable trigonal bipyramid²⁷ and if the resulting ions belong to the energetically more favorable octahedral or tetrahedral type, we observe a strong tendency toward adduct formation. This explains the surprising fact that ClF_3O and ClF_3 tend to form stable adducts with both Lewis acids and Lewis bases. The converse should also hold; *i.e.*, octahedral or tetrahedral molecules should show a weak tendency to form ions belonging to the trigonal-bi-

pyramid type. This has been noted for IOF_5 which does not form an adduct with SbF_5 ³⁹ and for ClO_2F which forms only a marginally stable adduct with CsF .^{28,29} Chlorine pentafluoride and ClF deserve special mention for the following reasons. ClF_5 does not form any adducts with strong Lewis bases.¹⁶ This is most likely due¹⁶ to a limitation of the coordination number of pentavalent chlorine to six (counting the free, sterically active electron pair as a ligand). Chlorine monofluoride forms with Lewis acids only 2:1 adducts.²¹ This can be explained by the instability of a hypothetical Cl^+ cation which would possess only an electron sextet. The relatively high stability of the ClF_2^- anion in spite of its trigonal-bipyramid type structure may be due to its high symmetry.^{37,38}

In summary, it is difficult to understand and predict relative acid–base properties of amphoteric halogen fluorides on the basis of the properties of the molecule itself. However, comparison of the structural stability of the parent molecule with that of the corresponding ions allows a qualitative interpretation. A method of predicting the structure of unknown halogen fluoride ions and molecules has previously been discussed⁴⁰ and should be particularly useful here.

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