RbF in BeF_2 Førland[19] attempted to test these two models on the basis of the quoted cryoscopic data of Roy, Roy, and Osborn.[16] Owing to the absence of reliable, independent information on the enthalpy of fusion and on the partial enthalpy of BeF_2, these attempts were not successful. More recently the same problem was considered by Mathews and Baes[14] on the basis of their heterogeneous equilibrium data. However, this work does not allow a reliable separation of the partial free energy data for BeF_2 into the appropriate enthalpy and entropy terms.

Figure 3 gives a comparison of the two "theoretical" excess entropy curves for models I and II with the experimental values. While the experimental uncertainties do not allow us to make a clear-cut choice between the two models at very low contents of LiF, the data show reasonable agreement with model I at intermediate contents of lithium fluoride, say between $N_{LiF} = 0.25$ and $N_{LiF} = 0.5$. In this range model II yields much too low values of the excess entropy.

Acknowledgments.—We are indebted to Drs. S. Cantor and C. F. Baes, Jr., of Oak Ridge National Laboratory for samples of distilled BeF_2 and for emf data on the BeF_2–LiF system made available prior to publication. The wet analyses of the samples of KF and RbF were carried out by Mr. M. E. Melnichak, who also checked the heat of fusion of BeF_2 by transposed temperature-drop calorimetry. This work has been supported by the National Science Foundation (GP-5015 and GP-7782) and by the Army Research Office, Durham, N. C. It has also benefited from the general support of Materials Science at the University of Chicago provided by the Advanced Research Projects Agency, Department of Defense.

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The FCl_2^+ Cation

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The FCl_2^+ cation, a new oxidizing species based on chlorine fluorides, has been prepared in the form of its AsF_6^- and BF_4^- salts. Chlorine monofluoride reacts with AsF_5 or BF_3 in a 2:1 mole ratio to form the FCl_2^+-containing salts. No evidence has been found for the existence of the Cl^+-containing 1:1 adducts reported previously for both the ClF–BF_3 and the ClF–AsF_5 systems. The results of the present investigation indicate that the actual 2:1 adducts may previously have been mistaken for 1:1 adducts. The $FCl_2^+AsF_6^-$ complex, a white crystalline solid, is stable at −78° and is completely dissociated in the gas phase at 25°. A pressure–temperature curve gives a heat of reaction, 32.83 kcal mol^{-1}, for the dissociation process: $FCl_2^+AsF_6^-(s) = 2ClF(g) + AsF_5(g)$. Reaction of solid $FCl_2^+AsF_6^-$ with NO_2F results in the quantitative displacement of 2 mol of ClF/mol of NO_2F and in the formation of a solid residue, $NO_2^+AsF_6^-$. Low-temperature infrared measurements on both salts, $FCl_2^+AsF_6^-$ and $FCl_2^+BF_4^-$, prove their ionic nature in the solid state. For FCl_2^+ all three fundamentals have been observed. They are split into several components by crystal field and ^{35}Cl–^{37}Cl isotope effects. Force constants based on a modified valence force field have been calculated for various structural models, bond angles, and assignments. From these data it is concluded that the most probable structure for FCl_2^+ is that of a symmetric, bent ion of symmetry C_{2v}. This ion has fluorine as a central atom and is isoelectronic with OCl_2. The FCl_2^+ cation can be considered as the first example of a polymeric halogen fluoride cation.

Introduction

Owing to their amphoteric nature, halogen fluorides can form (by combining with strong Lewis acids and bases) cations and anions containing one F^- ion less or more than the parent molecule. This group of compounds offers a unique chance to study the influence of the number of free electron pairs, of coordination number, and of a positive or negative charge at the central atom on the structure and bonding.[1] Recently, we have investigated the structure of ClF_2^-,[2–4] ClF_2^+,[5,6] ClF_4^-,[7,8] IF_4^+,[9] IF_6^-,[10] and IF_6^+.[11] The existence of the Cl^+ cation, derived from ClF by combination with strong Lewis acids, such as AsF_5 or BF_3, has been reported in 1963 by Schmeisser[12]

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[1] K. O. Christe, paper presented at the Fourth International Fluorine Symposium, Estes Park, Col., July 1967.

[2] K. O. Christe and J. P. Guertin, *Inorg. Chem.*, **4**, 905 (1965).

[3] K. O. Christe and J. P. Guertin, *ibid.*, **4**, 1785 (1965).

[4] K. O. Christe, W. Sawodny, and J. P. Guertin, *ibid.*, **6**, 1159 (1967).

[5] K. O. Christe and A. E. Pavlath, *Z. Anorg. Allgem. Chem.*, **335**, 210 (1965).

[6] K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 313 (1967).

[7] K. O. Christe and J. P. Guertin, *ibid.*, **5**, 473 (1966).

[8] K. O. Christe and W. Sawodny, *Z. Anorg. Allgem. Chem.*, **357**, 125 (1968).

[9] K. O. Christe and W. Sawodny, submitted for publication.

[10] K. O. Christe, J. P. Guertin, and W. Sawodny, *Inorg. Chem.*, **7**, 626 (1968).

[11] K. O. Christe and W. Sawodny, *ibid.*, **6**, 1783 (1967).

[12] M. Schmeisser, paper presented at the Symposium on Inorganic Fluorine Chemistry, Argonne, Ill., Sept 1963. For summary see *Science*, **143**, 1058 (1964).

based on the dissertation of Wenisch.[13] In this paper, we would like to report the preparation and identification of a new cation, FCl_2^+, derived from ClF, and our failure to confirm the existence of the 1:1 adducts between ClF and BF_3 or AsF_5 (supposedly containing the Cl^+ cation) reported by Schmeisser[12] and Wenisch.[13]

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-seasoned 304 stainless steel vacuum line equipped with Teflon FEP U traps and 315 stainless steel bellows-seal valves (Hoke Inc., 4251F4Y). Arsenic pentafluoride (from Ozark-Mahoning Co.) and BF_3 (from The Matheson Co., Inc.) were purified by several low-temperature vacuum distillations. Antimony pentafluoride (from Ozark-Mahoning Co.) was purified by vacuum distillation at ambient temperature. Hydrogen fluoride (from The Matheson Co., Inc.) was purified by removing all volatiles at −196° and exposing the residue at ambient temperature for 12 hr to a fluorine pressure of 2 atm. followed by removal of all volatiles at −196° *in vacuo*. Chlorine monofluoride and NO_2F (both prepared in this laboratory) were purified by fractional condensation. The purity of the starting materials was determined by measurements of their vapor pressures and infrared spectra. Owing to their hygroscopic nature, materials were handled outside the vacuum system under the dry nitrogen atmosphere of a glove box.

Preparation of $FCl_2^+AsF_6^-$.—In a typical experiment, ClF (96.7 mmol) and AsF_5 (24.2 mmol) were combined at −196° in a U trap. The mixture was allowed to warm up slowly until melting and reaction occurred. When the pressure inside the trap reached 760 mm, the mixture was cooled again to −196°. This procedure was repeated several times until the reaction was complete. Unreacted ClF (47.9 mmol) was recovered by distillation at −78°. Therefore, AsF_5 (24.2 mmol) had reacted with ClF (48.8 mmol) in a mole ratio of 1:2.02, producing the complex $FCl_2^+AsF_6^-$.

Similarly, synthesis of the complex $FCl_2^+AsF_6^-$ was achieved when an excess of AsF_5 (90.8 mmol) was combined with ClF (21.8 mmoles). Unreacted AsF_5 (79.0 mmol) was recovered by distillation at −78°. Therefore, ClF (21.8 mmol) had reacted with AsF_5 (11.8 mmol) in a mole ratio of 2:1.08.

Infrared measurements showed that the gas phase in equilibrium with the solid complex at temperatures −63.8 to −18.2° consisted of ClF and AsF_5 in a 2:1 mole ratio. (Intensity of the AsF_5 peak corresponded always to exactly one-third of the total sample pressure.)

A measured sample of the complex was slowly hydrolyzed in 2% NaOH. The solution was analyzed for arsenic (by atomic absorption spectroscopy) and chlorine (gravimetrically as AgCl following reduction to chloride). *Anal.* Calcd for Cl_2AsF_7: Cl, 25.4; As, 26.9. Found: Cl, 24.1; As, 27.9.

Preparation of $FCl_2^+BF_4^-$.—Chlorine monofluoride (51.2 mmol) and BF_3 (12.8 mmol) were combined at −196° in a U trap. The reaction was carried out similarly to that between ClF and AsF_5; however, the excess of ClF (25.2 mmol) was removed at −126°. Therefore, BF_3 (12.8 mmol) had reacted with ClF (26.0 mmol) in a mole ratio of 1:2.03.

The ClF–SbF_5 System.—Antimony pentafluoride (33.95 mmol) was transferred in the glove box to a Kel-F trap containing a Teflon-coated, magnetic stirring bar. The trap was connected to the vacuum line and 20 ml of liquid HF was condensed into the trap at −196°. The contents of the trap were warmed to ambient temperature and stirred until all SbF_5 had dissolved in the HF. Chlorine monofluoride (69.88 mmol) was condensed into the trap at −196°. The contents of the trap were allowed to warm up until the pressure inside the trap reached 1500 mm, followed by cooling to −196°. This procedure was repeated several times. Subsequently, the contents of the trap were kept for 12 hr at −78°. At the end of this period the pressure inside the trap had dropped to about 80 mm. The temperature of the trap was raised to −45° and all volatiles (HF and ClF) were removed *in vacuo*. The residue was a white solid showing yellow-orange patches. The weight (2.200 g) gained by the SbF_5 indicated a SbF_5 to ClF combining ratio of 1:1.19. The temperature of the trap was raised to 0° and additional volatile material was removed until no more vapor pressure above the solid could be detected. The weight (1.884 g) gained by the SbF_5 indicated at this point an SbF_5 to ClF combining ratio of 1:1.02. The temperature of the trap was raised to 23° and a pressure of 22 mm developed above the solid. The trap was disconnected from the vacuum line and transferred to the glove box. When the trap was opened, its contents had formed a brownish, viscous liquid.

In a second experiment SbF_5 (40.6 mmol) was placed into a passivated 95-ml Monel cylinder. Chlorine monofluoride (113 mmol) was added at −196°. The contents of the cylinder were allowed to warm to 23° and were kept at this temperature for 30 hr. Subsequently, the volatiles (61 mmol of ClF) were removed at 0° *in vacuo*, indicating an SbF_5 to ClF combining ratio of 1:1.28. When the temperature of the cylinder was raised to 23°, some additional ClF (5 mmol) was removed by pumping on the sample for 140 min, indicating an SbF_5 to ClF combining ratio of 1:1.12. Opening of the cylinders inside the glove box showed again a brownish, viscous liquid.

Dissociation Pressure Measurements.—The $AsF_5 \cdot 2ClF$ adduct was prepared in a Teflon FEP U trap being directly connected to a Heise, Bourdon tube-type gauge (0–1500 mm ± 0.1%). Pressures were read with a cathetometer (to an accuracy of ±0.2 mm) and 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 pressure before and after the pumping-off procedure was identical. Equilibrium pressures were always approached from below a given temperature.

Infrared Spectra.—The infrared spectra were recorded on a Beckman Model IR-7 with CsI interchange and a Perkin-Elmer Model 337 spectrophotometer in the range 700–200 and 4000–400 cm^{-1}, respectively. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. The spectra of solid $FCl_2^+AsF_6^-$ and $FCl_2^+BF_4^-$ were taken by preparing the complexes on the internal window (cooled with liquid nitrogen) of a low-temperature infrared cell. The body of this cell was made from Pyrex glass, all windows being AgCl in the range 4000–400 cm^{-1} and polyethylene (outer windows) and CsI (cold plate) in the range 700–200 cm^{-1}. The polyethylene and CsI windows were protected against chemical attack by several coatings of Halocarbon wax (from Halocarbon Products Corp., Series 10-00). To obtain a thin and uniform coating, the Halocarbon wax was dissolved in $CHCl{=}CCl_2$. Even using this technique a complete protection of the central CsI window could not be achieved in all experiments. Bands due to the window material were compensated by placing two wax-coated polyethylene windows into the reference beam. Warming up of the sample to the melting point of the starting materials followed by rapid cooling and pumping on the sample was essential to obtain good spectra of the solid complexes free of starting materials. Screw-cap metal cells with AgCl windows and Teflon FEP gaskets were used for obtaining the spectrum of NO_2^+-AsF_6^- as a dry powder at ambient temperature.

NO_2F-Displacement Reaction.—Nitryl fluoride (2.75 mmol) was combined with a large excess of solid $FCl_2^+AsF_6^-$ at −196° in a U trap. The mixture was allowed to warm up slowly. When the pressure inside the trap reached 760 mm, the mixture was cooled again to −196°. This procedure was repeated several times until the reaction was complete. All volatiles (5.33 mmol) were removed by distillation at −78° and were shown to be essentially pure ClF. Therefore, NO_2F had displaced ClF in a

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(13) F. Wenisch, Dissertation, Technische Hochschule, Aachen, Germany 1961.

mole ratio of 1:1.94. The excess of the $FCl_2^+AsF_6^-$ was removed at 25° from the trap leaving behind a white solid residue. This residue was identified as $NO_2^+AsF_6^-$ by its infrared spectrum.

Results

Synthesis.—Chlorine monofluoride and AsF_5, when mixed at −78°, produced the 2:1 complex FCl_2^+-AsF_6^-, a white, crystalline solid. Quantitative synthesis and elemental analysis of the solid complex, a quantitative displacement reaction with NO_2F, and infrared measurements on the gas phase above the solid complex clearly indicate a 2:1 combining ratio, the latter measurements showing that the complex is completely dissociated in the gas phase at 25°. This combining ratio was found independent of using either ClF or AsF_5 in excess. Similarly, ClF and BF_3, when mixed at −126°, produced the 2:1 complex $FCl_2^+BF_4^-$. Antimony pentafluoride, however, when combined with an excess of ClF either under high pressure or in HF solution did not produce a well-defined adduct.

Thermochemical Properties.—Based on the following observed data [temperature (°C), pressure (mm): −63.76, 1.7; −54.30, 6.0; −45.45, 16.5; −30.11, 68.5; −24.77, 120; −18.15, 209], a plot of log P_{mm} *vs.* T^{-1} (in °K) for the heterogeneous equilibrium

$$FCl_2^+AsF_6^-(s) = 2ClF(g) + AsF_5(g)$$

is a straight line. The equation $\log P_{mm} = 11.7124 - (2391.6/T)$ represents these dissociation data in the temperature range −63.8 to −18.2°. By extrapolation, a dissociation pressure of 1 atm was obtained at −2.4°. At 25° the dissociation pressure amounts to 4864 mm. From the slope of the log P_{mm} *vs.* T^{-1} curve, $\Delta H_d° = 32.83$ kcal mol^{-1} was found.[14] From $\Delta F°_T = -RT \ln Kp$ (atm), a free energy change, $\Delta F°_{298} = -2.16$ kcal mol^{-1}, and from $\Delta S°_T = (\Delta H° - \Delta F°_T)T^{-1}$, an entropy change, $\Delta S°_{298} = 117.41$ cal deg^{-1} mol^{-1}, were found for the dissociation process at 25°. A heat of formation of $FCl_2^+AsF_6^-(s)$, $\Delta H_f°_{298} = -355.4$ kcal mol^{-1}, was calculated based upon $\Delta H_f°_{298}[ClF(g)]^{15} = -13.5$ kcal mol^{-1} and $\Delta H_f°_{298}[AsF_5(g)]^{16} = -295.6$ kcal mol^{-1}.

The $FCl_2^+BF_4^-$ complex is stable at −127°, but shows a measurable dissociation pressure at −112°. Attempts to measure the dissociation pressure–temperature relation failed owing to difficulties in attaining equilibrium.

NO_2F Displacement Reaction.—Nitryl fluoride displaced ClF from solid $FlC_2^+AsF_6^-$ in a 1:2 mole ratio. The infrared spectrum of the solid reaction product showed (after removal of excess of $FCl_2^+AsF_6^-$) four absorptions at 2360, 696, 598, and 400 cm^{-1}, respectively.

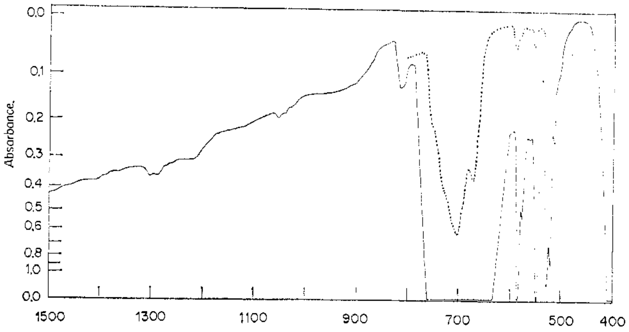

Figure 1.—Low-temperature infrared spectrum of solid FCl_2^+-AsF_6^- at two different concentrations in the range 1500–400 cm^{-1}; window material AgCl.

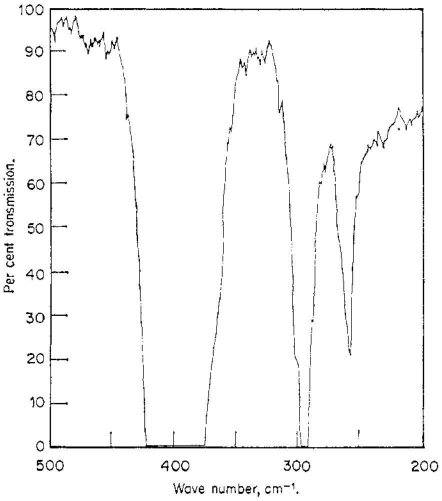

Figure 2.—Low-temperature infrared spectrum of solid FCl_2^+-AsF_6^- in the range 500–200 cm^{-1}; window material Halocarbon wax coated CsI and polyethylene.

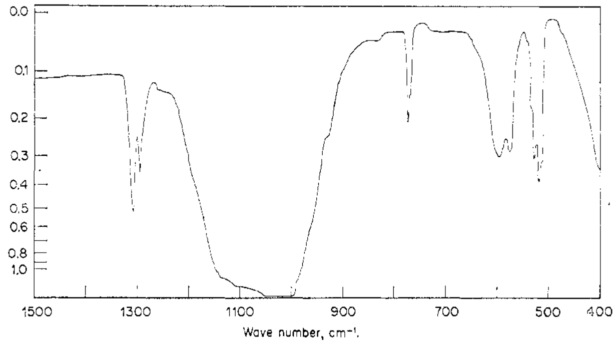

Figure 3.—Low-temperature infrared spectrum of solid FCl_2^+-BF_4^-; window material AgCl.

Infrared Spectra.—Figures 1 and 2 show the low-temperature infrared spectrum of solid $FCl_2^+AsF_6^-$ in the ranges 1500–400 and 500–200 cm^{-1}, respectively. Figure 3 shows the low-temperature infrared spectrum of solid $FCl_2^+BF_4^-$. The observed frequencies are listed in Table I. The absence of solid ClF, AsF_5, or BF_3 in the spectra can be readily established by com-

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(14) 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, $\Delta H_d°$ will be used throughout the text to mean the heat of reaction of a complete dissociation process of the type: complex(s) = gas + gas.

(15) "JANAF Interim Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1961.

(16) P. A. G. O'Hare and W. N. Hubbard, *J. Phys. Chem.*, **69**, 4358 (1965).

TABLE I

INFRARED SPECTRA OF $FCl_2^+AsF_6^-$ AND $FCl_2^+BF_4^-$ AND THEIR ASSIGNMENT

Obsd freq, cm^{-1}		Assignment (point group)		
$FCl_2^+BF_4^-$	$FCl_2^+AsF_6^-$	FCl_2^+ (C_{2v})	BF_4^- (T_d)	AsF_6^- (O_h)
	1312 1297 vw			$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$)
1308 1293 mw			$\nu_1 + \nu_4$ (F_2)	
1150–950 vs, b			ν_3 (F_2)	
	1058 vw	$2\nu_1$ (A_1)		
	828 w			$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$)
770 mw			ν_1 (A_1)	
	703 vs			ν_3 (F_{1u})
594 m	593 m	ν_3 (B_1)		
588 w, sh	586 mw			
	569 vw	$2\nu_2$ (A_1)		
572 mw	555 m			
532 mw, sh	535 m			
528 mw	527 mw	ν_1 (A_1)	ν_4 (F_2) B^{10}	
519 m	520 vw		ν_4 (F_2) B^{11}	
511 w, sh	514 vw, sh			
	397 ms			ν_4 (F_{1u})
	293 m	ν_2 (A_1)		
	258 mw			

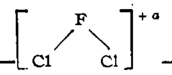
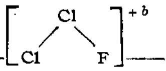
tion. However, a good approximation of the values of the General Valence Force Field was obtained in many cases.[19-22] For FCl_2^+ 586, 529, and 293 cm^{-1} were used as vibrational frequencies. Since no exact structural data are known for FCl_2^+, force constant sets were calculated for two different models: (i) a symmetric model with fluorine as the central atom and (ii) an asymmetric model with chlorine as the central atom. For each model the bond angle was varied between 90 and 180°. The results from these calculations are listed in Table II. For comparison, the force constants of Cl_2O were calculated by the same method[19] and show close agreement with the values of the General Valence Force Field[23,24] (see Table III).

Discussion

Synthesis and Properties.—The reaction conditions used in our synthesis of $FCl_2^+AsF_6^-$ and $FCl_2^+BF_4^-$

TABLE II

FORCE CONSTANTS OF FCl_2^+ FOR DIFFERENT MODELS AND BOND ANGLES

Bond angle, deg	Force constants, mydn/Å									
	 +a						 +b			
	f_r	f_{rr}	$\alpha_r f$	f_α	$f_{r(Cl-F)}$	$f_{R(Cl-Cl)}$	f_{rR}	$f_{r\alpha}$	$f_{R\alpha}$	f_α
90	2.26	−0.23	0.21	0.59	2.00	3.43	0.02	0.04	0.06	0.45
95	2.25	−0.11	0.21	0.56	1.99	3.44	0.02	0.04	0.06	0.43
100	2.26	0.02	0.20	0.52	2.01	3.42	0.03	0.04	0.06	0.42
105	2.27	0.14	0.20	0.49	2.04	3.39	0.06	0.03	0.06	0.40
110	2.30	0.26	0.19	0.46	2.08	3.35	0.11	0.03	0.05	0.39
115	2.34	0.39	0.17	0.43	2.12	3.32	0.17	0.02	0.05	0.38
120	2.40	0.52	0.16	0.40	2.16	3.31	0.24	0.01	0.04	0.36
130	2.54	0.79	0.12	0.34	2.24	3.34	0.41	0	0.02	0.33
140	2.75	1.08	0.09	0.29	2.33	3.41	0.58	−0.02	0	0.31
150	3.01	1.41	0.05	0.25	2.42	3.52	0.74	−0.03	−0.02	0.29
160	3.29	1.75	0.02	0.22	2.52	3.63	0.89	−0.03	−0.02	0.27
170	3.54	2.02	0	0.20	2.58	3.72	1.00	−0.02	−0.02	0.26
180	3.64	2.13	0	0.19	2.61	3.75	1.04	0	0	0.25

[a] Based on symmetry C_{2v}, ν_1 (A_1) = 529 cm^{-1}, ν_2 (A_1) = 295 cm^{-1}, and ν_3 (B_1) = 586 cm^{-1}. [b] Based on symmetry C_s, ν_{Cl-Cl} = 586 cm^{-1}, ν_{Cl-F} = 529 cm^{-1}, and $\delta_{Cl-Cl-F}$ = 295 cm^{-1}.

parison with the spectra previously reported[2,5,17] for these compounds.

Calculation of Force Constants.—For the calculation of force constants for FCl_2^+, the *G* and *F* matrices were set up according to the method of Wilson, Decius, and Cross,[18] assuming a valence force field. For the solution of the secular equation, a recently published method[19] was used. This allowed the calculation of a complete set of force constants without additional data except for the normal frequencies. Since more constants were calculated than frequencies were available, the method must be considered as an approxima-

TABLE III

COMPARISON OF FORCE CONSTANTS (MDYN/Å) OF OCl_2 AND FCl_2^+

	OCl_2 (GVFF)[a]	OCl_2 (GVFF)[b]	OCl_2[c]	FCl_2^+[c]
f_r	2.75	2.88	2.85	2.30 ± 0.10
f_{rr}	0.40	0.31	0.51	0.26 ± 0.26
$f_{r\alpha}$	0.15	0.17	0.18	0.19 ± 0.03
f_α	0.46	0.42	0.43	0.46 ± 0.06

[a] See ref 23. [b] See ref 24. [c] Present work; for method of calculation see ref 19.

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were very similar to those reported by Schmeisser[12] (based on the dissertation of Wenisch[13]) for the preparation of $Cl^+AsF_6^-$ and $Cl^+BF_4^-$. In the present investigation, however, only 2:1 adducts between ClF and AsF_5 or BF_3 were obtained independent of the mole ratio of the starting materials used in the synthesis. The composition of these complexes was well characterized by quantitative synthesis, elemental analysis, a quantitative displacement reaction with NO_2F, and infrared measurements on the solid adducts and on the gas phase above the solids. The absence of $Cl^+AsF_6^-$ as a stable intermediate in the thermal decomposition of $FCl_2^+AsF_6^-$ was proven by the following facts: (i) the dissociation pressure–temperature relation (plotted as log P *vs.* T^{-1}) is a straight line over the entire temperature range measured, (ii) the mole ratio of ClF to AsF_5 in the gas phase above the solid complex was 2:1 at all temperatures, and (iii) the first and last gas samples obtained from solid $2ClF \cdot AsF_5$ by exhaustive dissociation under mild conditions (vacuum, $-45°$) had the same 2:1 composition. Hence, it appears that Cl^+ (owing to its electron sextet) is considerably less stable than the FCl_2^+ species in which each atom has an electron octet. Whereas the formation of Cl^+ as a short-lived intermediate in the formation and thermal decomposition of $FCl_2^+AsF_6^-$ is possible, the existence of a relatively stable and well-defined $Cl^+AsF_6^-$ or $Cl^+BF_4^-$ (as reported previously[12,13]) could not be confirmed. All data, except for elemental analysis, obtained by Wenisch[13] are of qualitative nature and can be explained by either a 1:1 or a 2:1 adduct between ClF and BF_3 or AsF_5. Furthermore, the properties reported by Wenisch[13] for the 1:1 adducts are close to those obtained in the present investigation for the 2:1 adducts and some discrepancies exist in his analytical data (for example, for the ClF–AsF_5 adduct, the As:F ratio is as follows: found, 1:7.25; calcd for 1:1 adduct, 1:6; calcd for 2:1 adduct, 1:7). Therefore, it seems likely that the 1:1 adducts $Cl^+AsF_6^-$ and $Cl^+BF_4^-$ reported previously[12,13] were actually the 2:1 adducts $FCl_2^+AsF_6^-$ and $FCl_2^+BF_4^-$, respectively.

Both adducts $FCl_2^+AsF_6^-$ and $FCl_2^+BF_4^-$ are white solids and are stable at -78 and $-127°$, respectively, since they have no measurable vapor pressure or dissociation pressure at these temperatures. They do not appear to have any stable liquid state and are completely dissociated in the gas phase at 25°. Both adducts behave as powerful oxidizers toward iodide and most organic compounds and react violently with water.

The heat of dissociation,[14] 32.83 kcal mol^{-1}, obtained for $FCl_2^+AsF_6^-$ is of the same order of magnitude as the values obtained for similar ionic complexes such as $ClF_2^+BF_4^-$ (23.6 kcal mol^{-1})[25] and $NO^+ClF_2^-$ (15.5 kcal mol^{-1}).[2] The somewhat higher value for $FCl_2^+AsF_6^-$ is probably due to the difference between 1:1 and 2:1 adducts. Infrared measurements on the gaseous products from the dissociation of $FCl_2^+AsF_6^-$ indicated the presence of only ClF and AsF_5. Hence, the reaction $2ClF + AsF_5 \rightarrow FCl_2^+AsF_6^-$ is reversible and no new products such as possibly F_2Cl_2 are formed.

For the SbF_5–ClF system either a solvent such as HF or high pressure had to be used since the two starting materials do not have a common liquid range under normal conditions. In both cases a product was obtained having a varying composition and a melting point close to room temperature. Hence, no effort was made to investigate the exact nature of these adducts. The varying stoichiometry in the SbF–ClF system could possibly be due to the formation of dimeric or polymeric anions of the type $SbF_6^- \cdot xSbF_5$[26,27] and does not necessarily imply the presence of Cl^+ cations.

NO_2F Displacement Reaction.—When $FCl_2^+AsF_6^-$ was treated with NO_2F, the expected displacement of ClF by the stronger Lewis base NO_2F took place. The recovery of 2 mol of ClF/mol of NO_2F further supports the 2:1 combining ratio between ClF and AsF_5. The infrared spectrum of the solid residue showed the two bands characteristic for AsF_6^- [696 cm^{-1}, ν_3 (F_{1u}); 400 cm^{-1}, ν_4 (F_{1u})][11,28] and those reported for NO_2^+ [2360 cm^{-1} ν_3 (Σ_u^+) and 598 cm^{-1}, ν_2 (Π_u)].[29] Hence, the following reaction had taken place

$$FCl_2^+AsF_6^- + NO_2F \longrightarrow NO_2^+AsF_6^- + 2ClF$$

Infrared Spectra.—The 2:1 adducts between ClF and AsF_5 or BF_3 could be either fluorine-bridged coordination complexes or ionic species. The simplicity of the observed infrared spectra and the occurrence of all bands characteristic for AsF_6^- and BF_4^- suggest that the complexes are ionic. Table I shows the infrared spectra of $FCl_2^+AsF_6^-$ and $FCl_2^+BF_4^-$ together with their assignment. The vibrations belonging to AsF_6^- and BF_4^- can be easily assigned by comparison with the vibrational spectra of $K^+AsF_6^-$,[30] $NF_4^+AsF_6^-$,[18] $ClF_2^+AsF_6^-$,[6] $K^+BF_4^-$,[31-34] and $ClF_2^+BF_4^-$.[6] The observed frequencies and intensities are in good agreement.

The remaining bands observed in the spectra of both $FCl_2^+AsF_6^-$ and $FCl_2^+BF_4^-$ complexes should be due to the FCl_2^+ cation. This cation could have either fluorine or chlorine as a central atom and could be either bent or linear, symmetric or asymmetric. Thus, the following structures are possible

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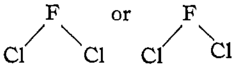
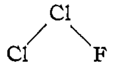
Cl—F—Cl
I

Cl—F-Cl
II



III

Cl—Cl—F
IV



V

All five models should exhibit three fundamental vibrations of which two are stretching vibrations and one is a deformation vibration. Model I (belonging to point group $D_{\infty h}$) is the only structure having a symmetry center. Therefore, only one of the two stretching vibrations should be infrared active for model I assuming that the selection rules apply strictly. For models II–V all three fundamentals are expected to be infrared active. The data of Table I (observation of at least two stretching vibrations at about 590 and 530 cm^{-1}, respectively, and one deformation vibration at about 290 cm^{-1}) thus rule out model I. Distinction between the linear structures (II and IV) and the bent structures (III and V) can be made on the following basis. If the central Y atom in linear X–Y–Z is not much heavier than the X and Z atoms, strong coupling should occur between the X–Y and Y–Z oscillators in a linear combination resulting in a large frequency separation of the two stretching modes.[22] For a bent, triatomic species the coupling and hence the frequency difference between the two stretching vibrations should decrease with decreasing bond angle. This effect has previously been demonstrated for the linear $[F–Cl–F]^-$ ($\Delta\nu$ = 160 cm^{-1})[4] and the bent $[F–Cl–F]^+$ ($\Delta\nu$ = 8 cm^{-1})[6] ions. For the linear models II and IV of FCl_2^+, $\Delta\nu$ should be even larger than for ClF_2^- owing to the different mass ratio between the central atom and the ligands. Consequently, the frequency difference of about 60 cm^{-1}, observed for FCl_2^+, renders the linear models II and IV highly improbable. This finding is also confirmed by the results from the force constant calculations (see below).

Distinction between the two remaining bent models (III and V) is more difficult; however, the following arguments favor structure III. Model V could be derived from ClF_2^+ by replacing one fluorine atom by chlorine. Hence, its Cl–F stretching vibration should occur in the same frequency range as that of ClF_2^+[6] and ClF,[35] *i.e.*, around 800 cm^{-1}. However, the highest frequency which can be assigned to FCl_2^+ was found at 594 cm^{-1}. Such a strong frequency decrease could only be explained by a large increase in the polarity of the Cl–F bond in FCl_2^+ when compared to that in ClF_2^+ or ClF. There are several examples of highly polar X–F bonds in YXF_n-type molecules such as ONF,[36] ONF_3,[37,38] and O_2F;[39] however, in all of these cases the Y–X bond has a high bond order thus compensating for the electron deficiency on the central atom. For FCl_2^+ only a slight frequency increase of the Cl–Cl stretching vibration was observed when compared to that of Cl_2,[40] even if the higher frequency at 586 cm^{-1} is assigned to this mode in FCl_2^+. Hence, model V containing a highly polar Cl–F bond is very unlikely.

On the other hand, model III having fluorine as the central atom is isoelectronic with OCl_2, and the infrared spectrum of FCl_2^+ is similar to that reported for OCl_2 (ν_3 686 cm^{-1}, ν_1 640 cm^{-1}, and ν_2 300 cm^{-1}).[23,41] The fact that the fundamental vibrations of FCl_2^+ occur at frequencies slightly lower than those of OCl_2 is somewhat unexpected. Usually, an increase of the positive charge on the central atom results for isoelectronic species in a frequency increase.[42] However, an exception to this rule has previously been observed[28] for the isoelectronic series BF_4^-, CF_4, and NF_4^+ and was explained by an increasing bond polarity. This argument may also be valid in the case of OCl_2 and FCl_2^+.

Distinction between the symmetric form (point group C_{2v}) and the asymmetric form (point group C_s) of model III cannot be made based on the infrared spectrum. However, the analogy to OCl_2 makes the symmetric form more likely, and, consequently, the assignment for FCl_2^+ in Table I was made for point group C_{2v}. Should FCl_2^+ actually be distorted (possibly due to crystal field effects), all conclusions will remain valid except for changing in Table I the point group and symmetry species for FCl_2^+. The sequence of ν_1 and ν_3 of FCl_2^+ was chosen by analogy with OCl_2. This assignment is further supported by the relative intensity of the 590- and the 530-cm^{-1} bands in $FCl_2^+BF_4^-$.

Several features of the infrared spectra are yet unexplained. (i) For $FCl_2^+BF_4^-$ the symmetric FCl_2^+ stretching vibration occurs in the same frequency range as the antisymmetric deformation mode of BF_4^-, thus making an assignment of the individual bands somewhat uncertain. (ii) The appearance of an additional band of relatively high intensity at 555 and 572 cm^{-1} in $FCl_2^+AsF_6^-$ and $FCl_2^+BF_4^-$, respectively, is possible owing to Fermi resonance between $2\nu_3$ (A_1) and ν_1 (A_1) of FCl_2^+. The band at 572 cm^{-1} in $FCl_2^+BF_4^-$ may contain some contribution from solid ClO_2F, present as trace impurity (as evident from the very weak bands at about 830 and 1250 cm^{-1}); however, ClO_2F alone could not account for the observed intensity of the 572-cm^{-1} band. Furthermore, the spectra of both $FCl_2^+AsF_6^-$ and $FCl_2^+BF_4^-$ may contain very weak contributions from bands due to ClO_2^+ (1298, 1284, 1046, 558, and 521 cm^{-1}).[43] In the case of $FCl_2^+AsF_6^-$ the 555 and 676 cm^{-1} band could also

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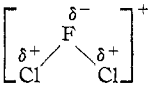
be due to ν_2 (E_g) and ν_1 (A_{1g}), respectively, of AsF_6^- having become infrared active owing to crystal field effects. (iii) The ν_3 (B_1) and ν_1 (A_1) bands of FCl_2^+ show splitting which most likely is due to the two chlorine isotopes ^{35}Cl and ^{37}Cl. (iv) The deformation vibration of FCl_2^+ shows a splitting into two bands at 293 and 258 cm^{-1}, respectively. This splitting is most likely due to crystal field effects and may be interpreted as a coupling effect of more than one FCl_2^+ group within the unit cell of the crystal. Attempts to record the infrared spectrum of $FCl_2^+BF_4^-$ below 400 cm^{-1} were unsuccessful. The occurrence of strong crystal field effects in both the $FCl_2^+AsF_6^-$ and the FCl_2^+-BF_4^- complexes is further evidenced by ν_1 (A_1) of BF_4^- becoming infrared active and by the appearance of two shoulders for ν_3 (F_{1u}) of AsF_6^-. The ν_2 (E_g) mode of AsF_6^- may also have become infrared active but is probably hidden by ν_3 of FCl_2^+. Explanations for these effects have been given previously for ClF_2^+-AsF_6^- and $ClF_2^+BF_4^-$.[4] (v) The only band yet unexplained occurs in the spectrum of $FCl_2^+AsF_6^-$ at 1058 cm^{-1} and is of very low intensity. Since its frequency is too high and its intensity too low for a fundamental vibration, it is assigned to $2\nu_1$ (A_1) of FCl_2^+.

Force Constants.—Table II shows the force constants calculated for different models. For the asymmetric model V, 586 cm^{-1} was assumed to be the Cl–Cl stretching vibration frequency, and 529 cm^{-1}, the corresponding Cl–F mode. A reversal of this assignment results in only a slight increase of the Cl–F valence force constant, $f_{r(Cl-F)}$, ranging from 2.34 to 2.64 mdyn/Å depending upon the bond angle. These values are still much lower than those obtained for ClF (4.36 mdyn/Å)[35] and ClF_2^+ (4.77 mdyn/Å).[6] The range of the Cl–Cl valence force constant, $f_{R(Cl-Cl)}$, changes to 2.80–3.71 mdyn/Å upon reversal of the assignment and thus shows in the most probable range of the bond angle (90–130°) a value lower than that found for Cl_2 (3.20 mdyn/Å).[40] The data of Table II show that the Cl–Cl valence force constant is increased only slightly in comparison with that of Cl_2, even if the higher frequency, 586 cm^{-1}, is assigned to ν(Cl–Cl). However, for bond angles smaller than 140° the Cl–F valence force constant would have a value lower than any previously found for Cl–F bonds. For ClF_2^- a value of 1.35 mdyn/Å was found for $f_{r(Cl-F)}$, but the bonding in this anion contains strong contributions from semiionic, three-center, four-electron bonds.[4] In the case of asymmetric FCl_2^+ and similar molecules or ions, such as ClF or ClF_2^+, in which the central atom has an electron octet, the formation of semiionic, three-center, four electron bonds is extremely unlikely[1] and, consequently, $f_{r(Cl-F)}$ should have a value larger than 4 mdyn/Å.

For the symmetric model III, bent $[Cl-F-Cl]^+$, bond angles smaller than 100° are unlikely since they result in negative values for the coupling constant f_{rr}. Similarly, bond angles larger than 120° are unlikely since the values for f_{rr} become too high. Hence, for FCl_2^+ the most probable set of force constants is: $f_r = 2.30 \pm 0.10$, $f_{rr} = 0.26 \pm 0.26$, $f_{r\alpha} = 0.19 \pm 0.03$, and $f_\alpha = 0.46 \pm 0.06$ mdyn/Å. For this set the bond angle was assumed to be 110° by analogy with OCl_2[22] and the uncertainty values were obtained from Table II assuming for the lower and upper limits of the bond angle values of 100 and 120°, respectively. The value of 100° assumed for the lower limit of the bond angle is probably too conservative. It seems to be more realistic to choose the bond angle of OCl_2 (110°) as the lower limit for FCl_2^+ since the size of the atoms is about the same for FCl_2^+ and OCl_2 but the increased positive charge on the chlorine ligands in FCl_2^+ is likely to result in an increased repulsion between the two chlorine atoms. Hence, the above given uncertainty values could be further reduced by assuming a bond angle of 115° for FCl_2^+ and by choosing values of 110 and 120° for the lower and upper limits, respectively, of the Cl–F–Cl bond angle. In order to test the reliability of the approximating method[19] used in our calculation for FCl_2^+, force constants were calculated also for OCl_2 and are compared (see Table III) with those obtained for a General Valence Force Field (GVFF) on the basis of additional data.[23,24] It can be seen that our approximating method[19] resulted in values very close to those of the GVFF. Consequently, also the values obtained for FCl_2^+ should be reliable within narrow limits.

Table III furthermore shows that the force constants obtained for FCl_2^+ are in fair agreement with those of isoelectronic OCl_2. The fact, that the valence force constant of FCl_2^+ has a value somewhat lower than that of OCl_2 is unexpected. It can be rationalized, however, assuming for FCl_2^+ the following high degree of polarization



The additional positive charge in FCl_2^+, when compared with isoelectronic OCl_2, will increase the polarity of the bonds and thus decrease the valence force constant. The bonding and force constants of FCl_2^+ are not comparable to those of the other known chlorine fluorides since FCl_2^+ is the only species having fluorine as the central atom and chlorine as the ligand.

The preferred formation of bent $[Cl-F-Cl]^+$ when compared to bent $[Cl-Cl-F]^+$ is not surprising. An intermediately formed Cl^+ cation, having only an electron sextet, will act as a strong Lewis acid. It can be expected to stabilize by combining with the atom acting as the strongest electron donor or Lewis base. In ClF the Cl–F bond is polarized in such manner that F owing to its higher electronegativity carries a partial negative charge. Hence, Cl^+ should combine with the fluorine atom and not with the chlorine atom of F–Cl to form the bent symmetric cation $[Cl-F-Cl]^+$. The reaction $2ClF + AsF_5 \rightarrow Cl_2F^+AsF_6^-$ resembles to some extent the well-known reaction between HF and strong Lewis acids, such as AsF_5

$$2HF + AsF_5 \longrightarrow H_2F^+AsF_6^-$$

In both cases, the electron-deficient cation (Cl^+ and H^+, respectively) is stabilized by adding one molecule of ClF or HF, respectively, to form a bent triatomic cation having fluorine as the central atom.

The FCl_2^+ cation is unusual for two reasons. (i) It is the first known interhalogen compound in which the most electronegative atom is the central atom. In all previously known interhalogen compounds the atom having the lowest electronegativity had always been the central atom. (ii) It is the first known example of a polymeric interhalogen cation.[44] It should be possible to prepare a whole new class of similar interhalogen cations (such as $Y-Y-Y^+$, $Y-Y-Z^+$, and $Y-X-Z^+$), by reaction of halogen fluorides with strong Lewis acids in the presence of halogen or interhalogen molecules suitable for stabilization of the halogen cation formed as an intermediate. Certain analogies exist between these hypothetical cations and the known $Y-Y-Y^-$, $Y-Y-X^-$, and $Y-X-Z^-$ interhalogen anions in which the Y^-, X^-, or Z^- anion is stabilized by the addition of a halogen (Y_2) or interhalogen (Y–X) molecule, respectively. For example, the I_3^-, I_2Br^-, and $BrICl^-$ anions have recently[45] been characterized by vibrational spectroscopy. In both, the triatomic polyhalogen anions and cations, the original monatomic ion is located in a terminal position. The basic difference between these cations and the anions is that the X^+ cation combines with the more electronegative part of the halogen or interhalogen molecule to form a bent cation. In the resulting triatomic cation the central atom has an electron octet (considering only the valence electrons) and a formal oxidation number of -1. In contrast, the X^- anion will combine with the more electropositive part of the halogen or interhalogen molecule to form a linear anion. In the resulting triatomic anion the central atom has an electron decet and a formal oxidation number of $+1$.

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Infrared and Raman Studies of Nitrate Impurity in Nitrite Complexes

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Infrared and Raman analyses are proposed for the determination of nitrate impurity in hexanitronickelate(II) complexes. Vibrational bands characteristic of the NO_3^- impurity in the complexes can be assigned. The infrared spectra of the complexes $K_4Ni(NO_2)_6$, $K_4Ni(NO_2)_6 \cdot H_2O$, and $K_2BaNi(NO_2)_6$ and spectral changes observed on heating the hydrate are discussed. High-quality infrared spectra were obtained using multiple attenuated total reflectance techiques (MATR).

Introduction

In a recent publication[1] we have shown that the relatively high absorptivities of the $\nu_2(A'')$ and $\nu_3(E')$ modes of the NO_3^- ion in infrared spectra, *ca.* 827 and 1387 cm^{-1}, respectively, permit detection and analysis of NO_3^- in the presence of NO_2^- for NO_3^- to NO_2^- ion ratios as low as 0.002. Vibrational bands attributed to various nitro and nitrito transition metal complexes are often reported in this spectral region. The possibility that vibrational bands due to NO_3^- may contribute to the observed spectrum of the complexed nitrite has generally been neglected. One might suspect NO_3^- to interfere for several reasons: (a) KNO_2 is often used as a starting material in the preparation of nitrite complexes but the so-called reagent grade KNO_2 commercially available has been reported to contain 0.3–10% NO_3^- and is very difficult to purify,[2,3] (b) nitrite complexes are usually made in slightly acidic aqueous solutions[4,5] but the NO_2^- ion is unstable with respect to NO_3^- in acid solution,[6] (c) NO_3^- and NO_2^- ions have the same charge and similar size so NO_3^- might easily copre-

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