Contribution from Rocketdyne, a Division of North
American Rockwell, Canoga Park, California 91304

A Fluorine-19 Nuclear Magnetic Resonance Study of Chlorine Fluoride Cations

KARL O. CHRISTE*, JOHN F. HON, and DON PILIPOVICH

Received June 6, 1972

Fluorine-19 nuclear magnetic resonance spectra are reported for HF solutions of ClF_6^+, ClF_4^+, ClF_2^+, $ClO_2F_2^+$, and ClF_2O^+ and for NF_2O^+ salts. Several exchange processes between the cations and anions and the solvent were observed, depending on the temperature and the acidity of the solvent. The acidity of the HF solvent was varied by the addition of AsF_5. It is shown that ClF_6^+ is octahedral and splitting owing to both ^{35}Cl–F and ^{37}Cl–F spin–spin coupling has been observed for the first time. The spectrum of ClF_4^+ is analogous to that of SF_4, indicating similar structures for these two isoelectronic species. For each of the remaining chlorine fluoride cations, only one signal was observed, indicating the presence of equivalent fluorine ligands with chlorine quadrupole relaxation preempting the observation of ClF spin–spin coupling. Contrary to previous reports, NF_2O^+ shows a triplet of equal intensity and line width. Chemical shifts are given for ClF and $FClO_2$ in the liquid phase.

Introduction

Halogen fluorides are known[1] to form adducts with numerous Lewis acids. It has been shown by vibrational spectroscopy and in some instances by X-ray diffraction studies that these adducts are predominantly ionic in the solid state.[1] Raman spectra of HF solutions have been reported only for $IF_6^+AsF_6^-$ [2] and ClF_2O^+ salts.[3,4] Except for a recently published note on the ^{19}F nmr spectrum of $IF_6^+AsF_6^-$ in HF solution,[5] no high-resolution nmr data have been reported for halogen fluoride adducts. This lack of nmr data is due to rapid chemical exchange between most of these cations and the HF solvent[6] even at low temperatures. This chemical exchange, however, can be suppressed by acidification of the HF solvent as was recently reported for SF_3^+ salts[7] and $IF_6^+AsF_6^-$.[5] In this paper, we report the results of our ^{19}F nmr study on chlorine fluoride cations.

Experimental Section

The preparation and characterization of $ClF_6^+PtF_6^-$,[8] $ClF_4^+SbF_6^-$,[9] $ClF_2O^+AsF_6^-$,[10] $ClF_2O^+PtF_6^-$,[11] $NF_2O^+AsF_6^-$,[12] and $ClF_2O_2^+PtF_6^-$ [13] have previously been described. The adducts between ClF_3 and BF_3, AsF_5, or SbF_5 were freshly prepared using a Monel Teflon-FEP vacuum system. The material balances observed for the ClF_2^+ adducts deviated by less than 0.5% from those calculated for 1:1 adducts. The purification and handling of HF has previously been described.[2,4] Chloryl fluoride and ClF were prepared from $KClO_3$ and ClF_3 and from $Cl_2 + ClF_3$, respectively. Chlorine trifluoride (The Matheson Co.) and AsF_5 (Ozark Mahoning Co.) were purified by fractional condensation prior to their use.

Teflon-FEP tubes ($^1/_8$-in. i.d., 0.015-in. wall thickness) were used as sample containers. The stable solids were transferred into the passivated (with ClF_3) tubes in the dry N_2 atmosphere of a glove box. Their amount was determined by weighing and volumetrically measured amounts of AsF_5 and HF were added at −196° on the vacuum line. The tubes were closed by Hoke valves during the transfers and were heat-sealed under vacuum. The loaded Teflon tubes were inserted into standard glass nmr tubes and $CFCl_3$ was added as an external standard.

The ^{19}F nmr spectra were recorded at 56.4 MHZ on a Varian high-resolution nmr spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the side-band technique with an accuracy of ±1 ppm.

Results and Discussion

The observed ^{19}F nmr chemical shifts are given in Table I. Figure 1 shows the difference in temperature dependence between an acidified and nonacidified HF solution. Figure 2 shows the multiplet structures of several of the resonances. The following compounds were studied in both HF and HF–AsF_5 as a solvent: $ClF_2^+BF_4^-$, $ClF_2^+AsF_6$, $ClF_2^+SbF_6^-$, $ClF_5 \cdot 1.36SbF_5$, $ClF_6^+PtF_6^-$, $ClF_2O^+AsF_6^-$, $ClF_2O^+PtF_6^-$, $ClF_2O_2^+PtF_6^-$, and $NF_2O^+AsF_6^-$. For the ClF_2^+ and ClF_2O^+ salts, acidification of the HF solvent with AsF_5 was required to observe the resonance lines due to the cations. This acidification, however, causes rapid exchange between the anion and HF, thus resulting in a single line for the anion, HF, and AsF_5. Without AsF_5 addition, the anion resonances can be observed as separate lines, but only a single line is observed for the cation and HF. The fact that one of the lines contains, in addition to HF, the resonance due to either the anion or cation was substantiated by peak area measurements on samples of known composition, such as $ClF_2O^+AsF_6^-$ (see footnote *k* of Table I), the observed chemical shifts, and their temperature dependence. The solubility of the salt in HF decreases with decreasing temperature. Hence, cooling of the sample results in a pronounced chemical shift for the line due to HF and the ion exchanging with it, but not for that of the nonexchanging counterion. A similar dependence of the exchange mechanism on the acidity of the solvent has previously been observed by Azeem and coworkers for SF_3^+ salts.[7] By analogy with the SF_3^+ compounds, the rapid exchange between ClF_2^+ and HF in nonacidified HF might be explained by $ClF_2^+ + HF_2^- \rightleftarrows ClF_3 + HF$. The addition of AsF_5 suppresses the HF_2^- formation and, hence, the exchange between ClF_2^+ and HF, but enhances the exchange between AsF_6^- and HF according to $AsF_6^- + H_2F^+ \rightleftarrows AsF_5 + 2HF$. For the HF solutions of $ClF_2^+BF_4^-$, $ClF_2^+SbF_6^-$, $ClF_4^+SbF_6^-$, and HF–ClF_3 mixtures, Raman spectra were also recorded. For the ClF_2^+ and ClF_4^+ salts, all bands expected for the individual ions were observed. Their frequencies deviated by less than 10 cm^{-1} from those observed for the solid adducts but showed no splitting of bands or violations of the symmetry rules. This suggests that in both the solid state and HF solution, the same discrete ions are present and

---

(1) For a recent review on interhalogen cations, see R. J. Gillespie and M. J. Morton, *Quart. Rev., Chem. Soc.*, 25, 533 (1971).

(2) K. O. Christe, *Inorg. Chem.*, 9, 2801 (1970).

(3) R. Bougon, J. Isabey, and P. Plurien, *C. R. Acad. Sci., Ser. C*, 273, 415 (1971).

(4) K. O. Christe, E. C. Curtis, and C. J. Schack, *Inorg. Chem.*, 11, 2212 (1972).

(5) M. Brownstein and H. Selig, *Inorg. Chem.*, 11, 656 (1972).

(6) K. O. Christe and A. E. Pavlath, *Z. Anorg. Allg. Chem.*, 335, 210 (1965).

(7) M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, 47, 4159 (1969).

(8) K. O. Christe, *Inorg. Nucl. Chem. Lett.*, 8, 741 (1972).

(9) K. O. Christe and D. Pilipovich, *Inorg. Chem.*, 8, 391 (1969).

(10) K. O. Christe, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, 11, 2205 (1972).

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

(12) K. O. Christe and W. Maya, *Inorg. Chem.*, 8, 1253 (1969).

(13) K. O. Christe, *Inorg. Nucl. Chem. Lett.*, 8, 453 (1972).

Table I. ^{19}F Nmr Spectral Data of Chlorine Fluoride Adducts in HF and HF–AsF_5 Solutions

Sample compn (mole ratio)	Temp, °C	δ, ppm ($CFCl_3$ ext ref)	Assignment	Notes
HF	15	199.6	HF	*a*
	−65	194.8	HF	*a*
HF, AsF_5 (20:1)	15	189	HF, AsF_5	*a*
	−65	186	HF, AsF_5	*a*
HF, AsF_5 (4:1)	15	134	HF, AsF_5	*a*
	−65	129	HF, AsF_5	*a*
$ClF_2^+AsF_6^-$, HF	−10	167	HF, ClF_2^+	*b*
		64	AsF_6^-	*b*
$ClF_2^+AsF_6^-$, HF, AsF_5 (14:300:1)	40	152	HF, $ClF_2^+AsF_6^-$, AsF_5	*c*
	−15	181	HF, AsF_5, ClF_2^+	*d*
		67	AsF_6^-	*d*
	−75	195	HF, AsF_5	*a*
$ClF_2^+AsF_6^-$, HF, AsF_5 (21:300:6)	10, −40	171, 185	HF, AsF_5, AsF_6^-	*b*
		23, · · ·	ClF_2^+	*b*
$ClF_2^+AsF_6^-$, HF, AsF_5 (2:30:14)	38	87	HF, AsF_5, AsF_6^-	*c*
		26	ClF_2^+	*c*
	30, 0	87	HF, AsF_5, AsF_6^-	*c*
		22	ClF_2^+	*e*
	−10, −25, −40	96, 102, 107	HF, AsF_5, AsF_6^-	*c*
		22	ClF_2^+	*a*
	−50, −60	111	HF, AsF_5	*c*
$ClF_2^+SbF_6^-$, HF (2:27)	50	175	HF, ClF_2^+	*d*
		~110	SbF_6^-	*f*
	35, 10	175, 183	HF, ClF_2^+	*a*
	−30	194.5	HF	*a*
$ClF_2^+SbF_6^-$, HF, AsF_5 (2:24.4:3.2)	30	146	HF, AsF_5	*c*
		122	SbF_6^-	*d*
		23	ClF_2^+	*c*
	10, −30, −70	143, 146, 150	HF, AsF_5	*c*
		122, 122, 127	SbF_6^-, HF absorbed on solid ClF_2^+-SbF_6^-?	*d*
		23, 23, · · ·	ClF_2^+	*a*
$ClF_2^+BF_4^-$, HF (2:15)	20, −60	162	HF, $ClF_2^+BF_4^-$	*c*
ClF_5·1.36SbF_5, HF (1:13)	40	190	HF, $ClF_4^+SbF_6^- \times SbF_5$	*d*
	0, −30	195, 197	HF	*e*
		125	SbF_6^-, $Sb_2F_{11}^-$	*c*
		−265	ClF_4^+	*e*
ClF_5·1.36SbF_5, HF, AsF_5 (1:15:3)	0, −20, −60	133	HF, AsF_5, SbF_6^-, $Sb_2F_{11}^-$	*e*
		−265	ClF_4^+	*e*
	−80	−274	ClF_4^+ } axial and equatorial fluorines	*g*
		−256	ClF_4^+	
$ClF_6^+PtF_6^-$, HF (1:50)	30	198	HF	*a*
		−389	ClF_6^+	*g, h*
$ClF_6^+PtF_6^-$, HF, AsF_5 (1:50:12)	40, −60	130	HF, AsF_5	*c*
		−388	ClF_6^+	*g, h*
		320	PtF_6^{2-}?	*i*
$ClF_2O^+AsF_6^-$, HF (1:11.8)	30	170	HF	*f*
		67.5	AsF_6^-	*j*
	10, −30	195	HF	*a*
		68	AsF_6^-	*d*
$ClF_2O^+AsF_6^-$, HF, AsF_5 (1:10.6:2)	20, −60	133, 142	HF, AsF_5, AsF_6^-	*c*
		−273.7, −270.8	ClF_2O^+	*a, k*
$ClF_2O^+PtF_6^-$, HF (1:34)	25	201.2	HF	*a*
		−273.2	ClF_2O^+	*a*
$ClF_2O^+PtF_6^-$, HF, AsF_5 (1:19:3.2)	20, −60	145	HF, AsF_5	*a*
		−272	ClF_2O^+	*a*
		320	PtF_6^{2-}?	*i*
$ClF_2O_2^+PtF_6^-$, HF, AsF_5	30	135	HF, AsF_5	*a*
		−310	$ClF_2O_2^+$	*c*
$NF_2O^+AsF_6^-$, HF (1:14)	−45	190	HF	*c*
		69	AsF_6^-	*c*
		−331	NF_2O^+	*c*
$NF_2O^+AsF_6^-$, HF, AsF_5 (1:9:2)	30	125	HF, AsF_5	*c*
		−330	NF_2O^+	*g, l*

[a] Sharp singlet. [b] See Figure 1. [c] Broad singlet. [d] Very broad singlet. [e] Broad singlet becoming narrower with decreasing temperature. [f] Very, very broad line. [g] See Figure 2. [h] Two sets of quadruplets of equal intensity with $J_{^{35}ClF} = 337$ and $J_{^{37}ClF} = 281 \pm 2$ Hz. [i] Weak triplet with 1:4:1 peak area ratio and $J_{^{195}PtF} = 2090 \pm 10$ Hz. [j] Poorly resolved quadruplet of about equal intensity with $J_{^{75}AsF}$ of about 900 Hz. [k] Peak area measurements at 20° resulted for ClF_2O^+:HF, AsF_5, AsF_6^- in a ratio of 10:139 (calcd 10:133). [l] Sharp triplet of equal intensity with J_{NF} of 250 Hz.

that the additional splittings and symmetry rule violations observed for the solids are due to lowering of the site symmetry or slight distortion of the ions. If these additional splittings and symmetry rule violations were indicative of *strong* covalent fluorine bridges, one should observe more pronounced frequency shifts when comparing the spectra of the solids with those of the HF solutions. Furthermore, it demonstrates the difference in time scale between nmr and vibrational spectroscopy for chemical exchange reactions. Whereas, the exchange rate between HF and ClF_2^+

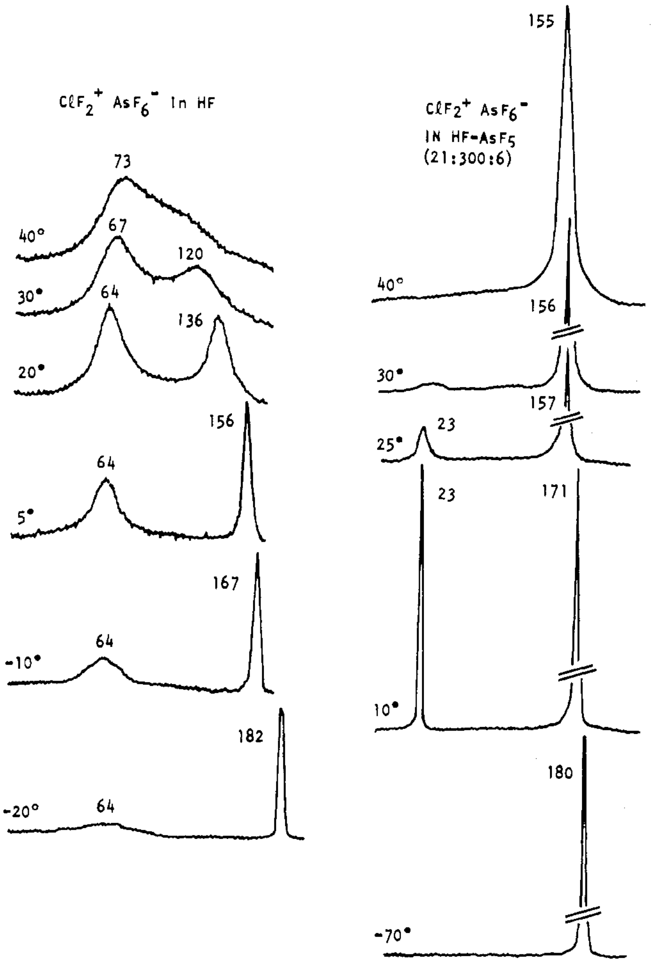


Figure 1. Temperature dependence of the ^{19}F nmr spectra of $ClF_2^+AsF_6^-$ in HF and HF-AsF_5 solution. Chemical shifts and temperatures are given in ppm from external $CFCl_3$ and °C, respectively.

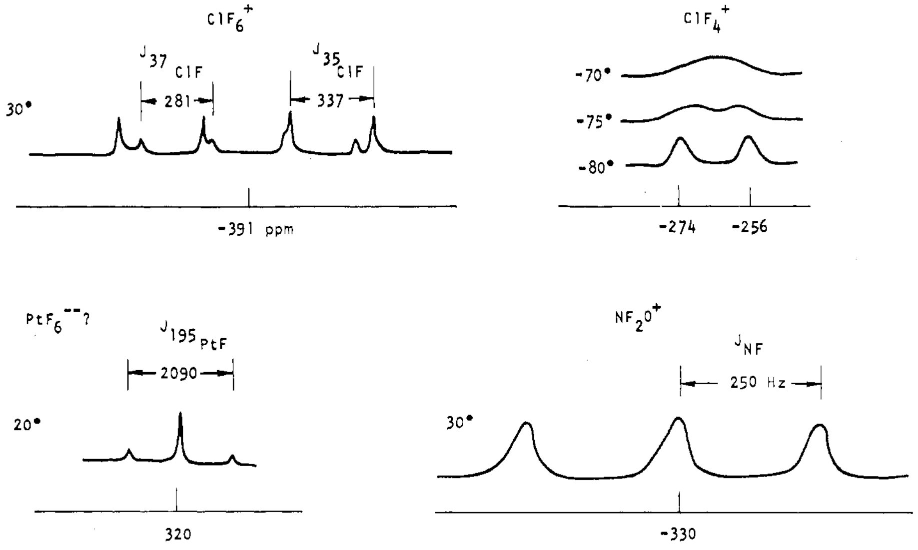


Figure 2. ^{19}F nmr spectra of several selected ions.

is fast enough to prevent observation of separate nmr signals, it is too slow to cause a collapse of the Raman lines. The Raman spectra of the HF-ClF_3 mixtures exhibited only the bands characteristic of ClF_3.[14] The absence of the characteristic ClF_2^+ lines[15,16] indicates that ClF_3 in HF is not ionized according to $ClF_3 + HF \rightarrow ClF_2^+ + HF_2^-$. However, this type of ionization has recently been demonstrated[3] for the structurally related ClF_3O molecule in HF solution.

In the following paragraphs, the individual compounds will be discussed in more detail.

ClF_2^+ Salts. Figure 1 demonstrates how acidification of the solvent and temperature variation influence the spectrum. Without acidification, only one broad line is observed above 40° due to rapid exchange between all three species, HF, ClF_2^+, and AsF_6^-. At 30°, separation into two peaks is noticeable. The chemical shift of one of the peaks (64 ppm) changes very little on further cooling, which suggests that the peak is due to AsF_6^-.[17,18] The chemical shift of the second peak steadily increases with decreasing temperatures and approaches at −60° that of pure HF. Evidently, this peak is due to rapidly exchanging ClF_2^+ and HF. The steady increase of the shift is caused by the decreasing solubility of $ClF_2^+AsF_6^-$ in HF with decreasing temperature as can also be seen from the decreasing relative intensity of the 64-ppm signal.

Solutions acidified with AsF_5 also show two peaks. The low-field resonance exhibits an almost temperature-independent shift of 23 ppm and is assigned to ClF_2^+. Above 30°, the line is extremely broad, while below 20° it is a sharp singlet which decreases in relative intensity with decreasing temperature owing to increasing precipitation of $ClF_2^+AsF_6^-$. The high-field resonance is due to rapidly exchanging HF, AsF_5, and AsF_6^-. Its chemical shift increases with decreasing temperature until essentially all of the AsF_6^- has precipitated. It then remains constant and corresponds to that expected for a HF-AsF_5 mixture.

Samples were studied containing different amounts of AsF_5 to determine how much AsF_5 was required to observe a separate line for ClF_2^+. When the HF contained 0.33 mole % AsF_5, no separate ClF_2^+ signal could be observed;

---

[14] H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, 52, 3517 (1970).

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

[16] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 9, 616 (1970).

[17] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 81, 1084 (1959); J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, 41, 1016 (1963).

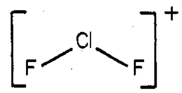
[18] K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, *Inorg. Chem.*, 6, 533 (1967).

however, addition of 2 mole % produced a separate ClF_2^+ line. Hence, the observation of a separate ClF_2^+ line cannot be caused by the formation of a stoichiometric adduct between AsF_5 and $ClF_2^+AsF_6^-$ or HF.

The spectra observed for $ClF_2^+SbF_6^-$ in HF and HF-AsF_5 solution are similar to those of the AsF_6^- salt. One difference was the observation of a broad signal for the HF-AsF_5 solution at about 120 ppm which is assigned to SbF_6^-.[7] Another effect was observed for the latter solution. With decreasing temperature, the solubility of $ClF_2^+SbF_6^-$ decreased as expected, and below −30° the signals attributable to ClF_2^+ and SbF_6^- had essentially disappeared. Further cooling to −70°, however, caused the HF solvent peak to become somewhat narrower and produced a new broad peak at 127 ppm. The intensity of the latter did not decrease with decreasing temperature. Based on its chemical shift, the temperature dependence of its intensity, and its absence in pure HF-AsF_5, it is tentatively assigned to HF bonded to the surface of the precipitated $ClF_2^+SbF_6^-$ salt by strong hydrogen bridges.

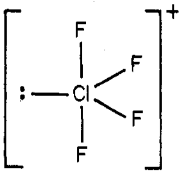
For $ClF_2^+BF_4^-$ in HF, only a single line was observed at 162 ppm between 20 and −60°. This lack of splitting into individual peaks might be explained by the low thermal stability of $ClF_2^+BF_4^-$ (1 atm dissociation pressure at 9°)[19] thus providing a ready anion-cation exchange mechanism, according to $ClF_2^+BF_4^- \rightleftarrows ClF_3 + BF_3$.

The observation of a sharp singlet for ClF_2^+ in its AsF_6^- and SbF_6^- salts is in excellent agreement with the bent structure of symmetry C_{2v}



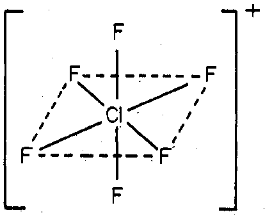
derived for this cation from single-crystal X-ray diffraction studies[20,21] and from vibrational spectroscopy.[15,16] In ClF_2^+, both fluorine ligands should be equivalent and chlorine quadrupole relaxation should preempt the observation of Cl-F spin-spin coupling. The change in chemical shift between ClF_3 and ClF_2^+ of +83 ppm is in the same direction as those observed for IF_7 and IF_6^+,[5] SF_4 and SF_3^+,[7] SF_4O and SF_3O^+,[22] and NF_3O and NF_2O^+,[23] though it is difficult to rationalize why cation formation does not generally result in increasing deshielding of the fluorine ligands.

The ClF_4^+ Cation. The $ClF_5 \cdot 1.36SbF_5$ adduct exhibits a broad resonance at −265 ppm in both HF and HF-AsF_5 mixtures at temperatures between 0 and −30°. Based on its chemical shift, it can be ascribed to a chlorine fluoride species containing chlorine in a high oxidation state. At lower temperatures, the solubility of $ClF_5 \cdot 1.36SbF_5$ in HF becomes very low. In HF-AsF_5, however, the solubility is sufficiently high to allow the observation of this signal in the range −70 to −80°. Below −70°, the −265-ppm resonance separates into a doublet of equal intensity with chemical shifts of −274 and −256 ppm (see Figure 2). This low-temperature splitting is analogous to that observed[17] by Muetterties and Phillips for isoelectronic SF_4. It strongly indicates the presence of a ClF_4^+ cation containing two pairs of nonequivalent fluorine ligands. These could rapidly exchange at higher temperatures by either an intermolecular[17] or an intramolecular pseudorotational Berry mechanism[24] to give a single peak. It was not possible (freezing point of HF) to lower the temperature sufficiently to observe the expected[17] triplet fine structure of the two resonances and to determine the F-F coupling constants. The observation of two pairs of nonequivalent fluorine ligands for ClF_4^+ agrees well with the structure of symmetry C_{2v}



suggested on the basis of vibrational spectra.[9,25] Due to the small difference in chemical shifts between the two ClF_4^+ resonances at −274 and −256 ppm, their assignment to the axial and equatorial fluorine atoms, respectively, should be considered tentative. This assignment is in line with the suggestion[26] by Muetterties and coworkers that in trigonal-bipyramidal species the axial fluorine ligands occur at a lower field than the equatorial ones.

The ClF_6^+ Cation. For salts containing the ClF_6^+ cation, two sharp sets of quadruplets of equal intensity were observed at −391 ppm in both HF and HF-AsF_5 solution (see Figure 2). The lack of exchange between ClF_6^+ and HF is not surprising since an equilibrium such as $ClF_6^+ + HF_2^- \rightleftarrows ClF_7 + HF$ is impossible owing to the nonexistence[8] of stable ClF_7. The peak area ratio between the two sets was 3:1, indicating that they are due to the ^{35}Cl and ^{37}Cl isotopes, having a natural abundance of 75.4 and 24.6%, respectively. The splitting of the signals into quadruplets of equal intensity can be explained by spin-spin coupling between Cl ($I = {}^3/_2$) and F. This Cl-F spin-spin coupling, however, is usually not observed for chlorine fluorides due to rapid relaxation caused by interaction of the chlorine quadrupole moment with an unsymmetric electric field gradient. Consequently, the observation of well resolved Cl-F spin-spin coupling for ClF_6^+ is strongly indicative of a spherically symmetric electric field about the Cl nucleus.



This confirms that indeed ClF_6^+ has symmetry O_h as suggested on the basis of its vibrational spectrum.[8] Previously, only one case of a partially resolved Cl-F spin-spin coupling was observed for $FClO_3$[27,28] which has an almost spherically symmetric electric field. For $FClO_3$, $J_{^{35}ClF}$ was

---

[19] H. Selig and J. Shamir, *Inorg. Chem.*, 3, 294 (1964).

[20] A. J. Edwards and R. J. C. Sills, *J. Chem. Soc. A*, 2697 (1970).

[21] H. Lynton and J. Passmore, *Can. J. Chem.*, 49, 2539 (1971).

[22] M. Brownstein, P. A. W. Dean, and R. J. Gillespie, *Chem. Commun.*, 9 (1970).

[23] C. A. Wamser, W. B. Fox, B. Sukornick, J. R. Holmes, R. B. Stewart, R. Juurik, N. Vanderkooi, and D. Gould, *Inorg. Chem.*, 8, 1249 (1969).

[24] R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960); *Rev. Mod. Phys.*, 32, 447 (1960).

[25] K. O. Christe, E. C. Curtis, D. Philipovich, C. J. Schack, and W. Sawodny, Paper B4, 6th International Symposium on Flourine Chemistry, Durham, England, July 1971; K. O. Christe and W. Sawodny, to be submitted for publication.

[26] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 3, 1298 (1964).

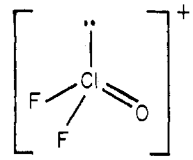
[27] S. Brownstein, *Can. J. Chem.*, 38, 1597 (1960).

[28] J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, 41, 3063 (1963).

estimated to be 310[27] or 289 Hz[28], but an estimate of $J_{^{37}\mathrm{ClF}}$ was preempted by large line widths. For $\mathrm{ClF_6^+}$, $J_{^{35}\mathrm{ClF}}$ and $J_{^{37}\mathrm{ClF}}$ are 337 and 281 ± 2 Hz, respectively. The observed ratio of $J_{^{35}\mathrm{ClF}} : J_{^{37}\mathrm{ClF}} = 1.199$ is in excellent agreement with the value of 1.202 calculated from the ratio of the magnetic moments of the two chlorine isotopes.[29] The observed full line width at half-height is only 15 Hz for $\mathrm{ClF_6^+}$, compared to about 430 Hz for $\mathrm{FClO_3}$.[27] This indicates that the electric field about the Cl nucleus in $\mathrm{ClF_6^+}$ is, as expected, much more spherical than that in $\mathrm{FClO_3}$. In addition, the center of the $\mathrm{^{37}ClF_6^+}$ resonance is shifted by 0.15 ± 0.02 ppm upfield from that of $\mathrm{^{35}ClF_6^+}$. This shift may be explained[30] by the difference in the vibrational amplitudes of the two Cl isotopes. The heavier isotope has a smaller vibrational amplitude causing the electrons of the fluorine atom to be less polarized and resulting in increased ^{19}F shielding. A similar change in chemical shift (0.053 ppm) in the same direction has been observed[31] for the isoelectronic $\mathrm{^{32}SF_6}$ and $\mathrm{^{34}SF_6}$ isotopes. The fact that the isotopic shift for $\mathrm{ClF_6^+}$ is several times larger than that for $\mathrm{SF_6}$ is in line with the observed large increase[31] from $\mathrm{SiF_6^{2-}}$ toward $\mathrm{SF_6}$.

In addition to the solvent lines, a weak resonance was observed in acidified HF at 320 ppm. This signal consists of a triplet showing a 1:4:1 peak area ratio and a coupling constant of 2090 ± 10 Hz (see Figure 2). These observations suggest that the resonance is due to a platinum species. Of the naturally occurring platinum isotopes, only ^{195}Pt (abundance 33.7%) has a nuclear spin ($I = {}^1/_2$). Spin-spin coupling between F and ^{195}Pt would result in two satellites, each with peak areas equal to one-fourth of that of the central peak. Assignment of the 320-ppm signal to $\mathrm{PtF_6^-}$ is unlikely for the following reasons: (1) its peak area is much too small when compared to those of the counterions, (2) no signal was observed in this range for other $\mathrm{PtF_6^-}$ salts, and (3) $\mathrm{PtF_6^-}$ is paramagnetic[32] and a large anisotropic downfield shift might be expected similar to that observed for $\mathrm{PtF_6}$ (−5550 and −3000 ppm).[33] Since $\mathrm{PtF_6^{2-}}$ is the only diamagnetic tetravalent or higher valent platinum fluoride, we tentatively assign the 320-ppm signal to this anion.

The $\mathrm{ClF_2O^+}$ Cation. The ^{19}F nmr spectra of both $\mathrm{ClF_2O^+AsF_6^-}$ and $\mathrm{ClF_2O^+PtF_6^-}$ show a sharp singlet at about −273 ppm, which is assigned to $\mathrm{ClF_2O^+}$. This indicates two equivalent fluorine atoms for $\mathrm{ClF_2O^+}$ in good agreement with the structure of symmetry C_s proposed[3,4] on the



basis of vibrational spectra. The remaining features of the spectra are analogous to those discussed above for $\mathrm{ClF_2^+}$ and $\mathrm{ClF_6^+}$ salts and, hence, are not reiterated.

The $\mathrm{ClF_2O_2^+}$ Cation. A sample containing about 10 mole % of $\mathrm{ClF_2O_2^+PtF_6^-}$ showed a broad, weak singlet at −310 ppm. Since it cannot be attributed to any known chlorine fluoride species, it is tentatively assigned to $\mathrm{ClF_2O_2^+}$.[33a] Its chemical shift and lack of splitting are consistent with the structure of symmetry C_{2v} as indicated by its vibrational spectrum.[13]

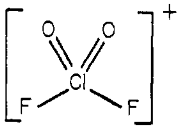


Table II. Summary of ^{19}Nmr Shifts and Coupling Constants of Liquid Chlorine Fluorides and Oxyfluorides and of Their Cations in HF Solution

Compd	Temp, °C	Chem shift, ppm (from ext $\mathrm{CFCl_3}$)	Coupling constant, Hz	Ref
ClF	−80	419.4		*a*
$\mathrm{Cl}F_2(\mathrm{F})$	−60	−114.3, −121.8, doublet	$J_{\mathrm{FF}} = 421$	*a–c*
$\mathrm{ClF_2}(F)$		−15.0, −7.7, −0.4, triplet		
$\mathrm{Cl}F_4(\mathrm{F})$		−247, doublet	$J_{\mathrm{FF}} = 130$	*d*
$\mathrm{ClF_4}(F)$		−412, quintet		
$\mathrm{ClF_3O}$	10	−262		*e*
$\mathrm{FClO_2}$	−80	−315		*a*
$\mathrm{FClO_3}$		−287, quartet	$J_{^{35}\mathrm{ClF}} = 289$	*f*
$\mathrm{ClF_2^+}$	10	23		*a*
$\mathrm{Cl}F_2(\mathrm{F_2})^+$	−80	−256		*a*
$\mathrm{ClF_2}(F_2)^+$	−80	−274		*a*
$\mathrm{ClF_6^+}$	40	−388, quartet	$J_{^{35}\mathrm{ClF}} = 337$, $J_{^{37}\mathrm{ClF}} = 281$	*a*
$\mathrm{ClF_2O^+}$	20	−272		*a*
$\mathrm{ClF_2O_2^+}$	30	−310		*a*

[a] Data from this study. [b] In addition to the first-order splitting, the −114.3, −121.8, and −7.7-ppm resonances show second-order splitting. [c] Reference 36. [d] D. Pilipovich, W. Maya, E. A. Lawton, H. F. Bauer, D. F. Sheehan, N. N. Ogimachi, R. D. Wilson, F. C. Gunderloy, Jr., V. E. Bedwell, *Inorg. Chem.*, 6, 1918 (1967). [e] D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, *Inorg. Chem.*, 11, 2189 (1972). [f] Reference 28; H. Agahigian, A. P. Gray, and G. D. Vickers, *Can. J. Chem.*, 40, 157 (1962).

The $\mathrm{NF_2O^+}$ Cation. The ^{19}F nmr spectrum of $\mathrm{NF_2O^+}$ has previously been reported[23] to consist of a partially resolved 4:5:4 triplet at −331 ppm with $J_{\mathrm{NF}} = 250$ Hz and the outer members of the triplet being broader than the central member. As can be seen from Figure 2, acidification with $\mathrm{AsF_5}$ of an HF solution of $\mathrm{NF_2O^+AsF_6^-}$ results in a well-resolved triplet of equal intensity and bandwidth as expected for $\mathrm{NF_2O^+}$. Whereas the previously reported[23] peak area ratio and relative line width are not confirmed, the observed chemical shifts and coupling constants are in excellent agreement.

Summary

Table II summarizes all presently known ^{19}F nmr spectra of chlorine fluorides and oxyfluorides and of their cations. As can be seen, data are now available for all compounds except for the very recently discovered[34] oxyfluoride $\mathrm{ClF_3O_2}$[34a] and the $\mathrm{Cl_2F^+}$ cation.[35] We have redetermined the chemical shifts of ClF and $\mathrm{FClO_2}$ in the liquid phase since only measurements on the gas have previously been report-

---

(29) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 188.

(30) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, England, 1966, Vol. 2, p 875.

(31) R. J. Gillespie and J. W. Quail, *J. Chem. Phys.*, 39, 2555 (1963).

(32) N. Bartlett and S. P. Beaton, *Chem. Commun.*, 167 (1966).

(33) R. Blinc, E. Pirkmajer, J. Slivnik, and I. Zupancic, *J. Chem. Phys.*, 45, 1488 (1966).

(33a) Note Added in Proof. The assignment of the −310-ppm signal to $\mathrm{ClF_2O_2^+}$ has in the meanwhile been confirmed for $\mathrm{ClF_2O_2^+BF_4^-}$ and $\mathrm{ClF_2O_2^+AsF_6^-}$ (K. O. Christe and E. C. Curtis), to be published.

(34) K. O. Christe, *Inorg. Nucl. Chem. Lett.*, 8, 457 (1972).

(34a) Note Added in Proof. $\mathrm{ClF_3O_2}$ shows a second-order splitting $\mathrm{AB_2}$ pattern centered at −413 ppm with $J_{\mathrm{FF}} = 443$ Hz and $J/\nu_0\delta = 1.0$ (K. O. Christe and R. O. Wilson), to be published.

(35) K. O. Christe and W. Sawodny, *Inorg. Chem.*, 8, 212 (1969).

ed.[36] In addition, we have redetermined the chemical shifts for liquid ClF_3 since there is some confusion in the literature[17,37,38] concerning its exact values. Most of the data of Table II can be qualitatively rationalized by assuming increasing deshielding of the fluorine ligands with increasing oxidation state of the chlorine central atom (see trends for ClF-ClF_3-ClF_5, ClF_2^+-ClF_4^+-ClF_6^+, or ClF_2O^+-$ClF_2O_2^+$). The effect of oxygen substitution is more difficult to understand. For example, the fluorine in $FClO_2$ is more deshielded than that in $FClO_3$. Also, the high shielding of F in ClF and the increased shielding in the cations when compared to their parent molecules are unexpected. Clearly, our present understanding of the nature of ^{19}F chemical shifts is insufficient to rationalize all these observations.

Registry No. HF, 7664-39-3; AsF_5, 7784-36-3; $ClF_2^+AsF_6^-$, 19154-21-3; $ClF_2^+SbF_6^-$, 30669-19-3; $ClF_2^+BF_4^-$, 36544-26-0; ClF_5, 13637-63-3; SbF_5, 7783-70-2; $ClF_6^+PtF_6^-$, 36609-91-3; $ClF_2O^+AsF_6^-$, 36544-27-1; $ClF_2O^+PtF_6^-$, 36544-28-2; $ClF_2O_2^+PtF_6^-$, 36609-92-4; $NF_2O^+AsF_6^-$, 25562-24-7; ClF, 7790-89-8; $FClO_2$, 13637-83-7; $FClO_3$, 7616-94-6; $ClF_2(F_2)^+$, 36544-30-6.

Acknowledgment. We are indebted to Dr. C. J. Schack and R. D. Wilson for their help and to the Office of Naval Research, Power Branch, for financial support.

(36) L. G. Alexakos and C. D. Cornwell, *J. Chem. Phys.*, 41, 2098 (1964).

(37) E. W. Lawless and I. C. Smith, "Inorganic High Energy Oxidizers," Marcel Dekker, New York, N. Y., 1968, p 20.

(38) C. H. Dungan and J. R. Van Wazer, "Compilation of Reported F^{19} NMR Chemical Shifts," Wiley-Interscience, New York, N. Y., 1970, No. 819.

Contribution from the Reactor Chemistry Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Fluoroborate Equilibria in Aqueous Solutions[1a]

R. E. MESMER,* K. M. PALEN,[1b] and C. F. BAES, Jr.

Received June 14, 1972

The stability of fluoroborate species has been examined in 1 *m* NaCl solution at 25° by means of potentiometric titrations in which the free fluoride ion concentration was measured with the LaF_3 electrode and the pH was measured with the hydrogen electrode. The procedure consisted of the addition of acid to 0.01 and 0.03 *m* boric acid containing 0.02-0.08 *m* NaF, with variation of the pH from 7 to 2. Under these conditions negligible amounts of BF_4^- ion, which forms only slowly, were produced. The results are explained by the following reactions and equilibrium quotients

$$\begin{aligned}
&B(OH)_3 + F^- \rightleftharpoons BF(OH)_3^- && \log Q = -0.36 \pm 0.2\\
&B(OH)_3 + 2F^- + H^+ \rightleftharpoons BF_2(OH)_2^- + H_2O && \log Q = 7.06 \pm 0.02\\
&B(OH)_3 + 3F^- + 2H^+ \rightleftharpoons BF_3OH^- + 2H_2O && \log Q = 13.689 \pm 0.003
\end{aligned}$$

Under the conditions of measurement, BF_3OH^- was the major species formed and the species $BF(OH)_3^-$ was barely detectable. Combined with other equilibrium quotients, known previously, these results give the following log *Q* values for the stepwise replacement of OH^- by F^- in the conversion of $B(OH)_4^-$ to BF_4^-: $-5.3 \pm 0.2, -6.3 \pm 0.2, -7.10 \pm 0.02, -8.40 \pm 0.1$. There was no evidence for the formation of the undissociated acids HBF_3OH or $HBF_2(OH)_2$ or for the formation of polyborate species.

The chemistry of fluoroborates has been extensively studied, largely as a result of the technological importance of BF_3 and its derivatives. The work prior to 1949 has been covered in the extensive review of Booth and Martin.[2] In aqueous solutions and in solids the ions BF_4^-, BF_3OH^-, and $B(OH)_4^-$ occur, and possibly the ions $BF_2(OH)_2^-$ and $BF(OH)_3^-$ as well. It is clear from the studies of Wamser,[3] Ryss, *et al.*,[4] and Sen Gupta and Mukherjee[5] that all such species, with the exception of BF_4^-, can undergo rapid and reversible interconversion in aqueous solution at room temperature.

The BF_4^- ion is well established as a stable species both in solid compounds and in aqueous solutions. Its stability toward hydrolysis in neutral or basic solutions is the basis for its determination in mixtures with the other more reactive fluoroborates.[3b] The X-ray studies by Clark and Lynton[6] and by Brunton[7] of crystalline alkali fluoroborates have shown that the BF_4^- ion is a slightly distorted tetrahedron. The Raman spectrum of BF_4^- in aqueous solutions[8,9] and in melts[8] similarly indicates a tetrahedral structure. Nuclear magnetic resonance spectra[10] of the aqueous ion reveal the number of lines and the fine structure for ^{19}F and ^{11}B couplings expected for a symmetrical ion with slow exchange of the fluorides.

Alkali and alkaline earth salts of BF_3OH^- were first prepared by Ryss and by Wamser. Clark and Lynton[11] have determined the crystal structure of $NaBF_3OH$ and also found the anion BF_3OH^- to be very nearly tetrahedral. The nmr

(1) (a) Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corp. (b) Summer trainee sponsored by Oak Ridge Associated Universities.

(2) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," Wiley, New York, N. Y., 1949.

(3) (a) C. A. Wamser, *J. Amer. Chem. Soc.*, 70, 1209 (1948); (b) *ibid.*, 73, 409 (1951).

(4) I. G. Ryss, *C. R. (Dokl.) Acad. Sci. URSS*, 54, 325 (1946); I. G. Ryss and M. M. Slutskaya, *Zh. Fiz. Khim.*, 21, 549 (1947); I. G. Ryss, M. M. Slutskaya, and S. D. Palevskaya, *ibid.*, 22, 1322 (1948); I. G. Ryss and M. M. Slutskaya, *J. Gen. Chem. USSR*, 22, 45 (1952).

(5) A. Sen Gupta and S. K. Mukherjee, *J. Indian Chem. Soc.*, 47, 679, 1189 (1970).

(6) M. J. R. Clark and H. Lynton, *Can. J. Chem.*, 47, 2579 (1969).

(7) G. Brunton, *Acta Crystallogr., Sect. B*, 24, 1703 (1968).

(8) A. S. Quist, J. B. Bates, and G. E. Boyd, *J. Chem. Phys.*, 54, 4896 (1971).

(9) J. Goubeau and W. Bues, *Z. Anorg. Allg. Chem.*, 288, 221 (1952).

(10) K. Kuhlmann and D. M. Grant, *J. Phys. Chem.*, 68, 3208 (1964).

(11) M. J. R. Clark and H. Lynton, *Can. J. Chem.*, 48, 406 (1970).