hydride and stored over molecular sieves. Ethanol was dried over P_4O_{10} and stored over molecular sieves. $CDCl_3$ and Me_4Si were purchased from MSD and Aldrich, respectively, and stored over molecular sieves. $AsCl_3$, Pr^iMgCl, (vinyl)MgCl, and PhMgCl were obtained from Strem Chemical Co. Et_3Al, $Pr^n{}_3Al$, $Bu^n{}_3Al$, and $Bu^i{}_3Al$, and $Bu^i{}_3Al$ were purchased from Ethyl Corp. and used as obtained.

$Pr^n{}_2Zn$ and $Bu^n{}_2Zn$ were synthesized by the slow, room-temperature addition of the stoichiometric amount of the appropriate trialkylalane to a suspension of anhydrous $Zn(C_2H_3O_2)_2$ (obtained from the commercial dihydrate with boiling acetic anhydride) in *n*-hexane. After the addition was complete, the reaction mixture was refluxed for 7 h, the solvent was distilled, and the dialkylzinc compound was purified by distillation on a spinning-band column: $Pr^n{}_2Zn$ (77 °C (56 Torr), 86% yield) and $Bu^n{}_2Zn$ (61 °C (4 Torr), 92% yield). The ^1H ($Pr^n{}_2Zn$[59] and $Bu^n{}_2Zn$[60]) and ^{13}C NMR ($Bu^n{}_2Zn$[60]) spectral data agreed with those previously reported. The ^{13}C spectral data (δ_C, ppm) for $Pr^n{}_2Zn$ are as follows: 19.27, ($CH_3CH_2CH_2As$); 19.78, ($CH_3CH_2CH_2As$); 21.12, ($CH_3CH_2CH_2As$).

OCH_2CH_2OAsCl and $OCMe_2CMe_2OAsCl$ were synthesized by using a slight modification of the previously described procedure.[61] The use of Et_3N, in place of pyridine, provided a better yield (62%). OCH_2CH_2OPCl was synthesized from the reaction of PCl_3 with ethylene glycol.[62]

General Synthesis of R_3As by the Reactions of RMgX (X = Cl, Br) and RLi with OCH_2CH_2OAsCl. In a typical synthesis, 0.06 mol of OCH_2CH_2OAsCl was added to 400 mL of Et_2O (*n*-hexane for the RLi reactions) in a 1-L three-necked, round-bottom flask fitted with a reflux condenser, a mechanical stirrer, and a pressure-equalizing addition funnel. A solution of 0.18 mol of the appropriate alkylating reagent was added slowly over a period of 2 h to the vigorously stirred chloroarsolane solution that was maintained at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. [In the case of $(mesityl)_3As$, the mixture was refluxed for 12 h. The RLi reactions were refluxed for 24 h.] Unreacted alkylating agent was then hydrolyzed with a degassed, saturated NH_4Cl solution. After the organic solvent layer, which contained the arsine, was isolated, the aqueous layer was extracted three times with 75 mL of Et_2O or *n*-hexane and the extracts were added to the initial solvent layer. The arsine-containing solution was dried over anhydrous Na_2SO_4. Following distillation of the solvent, the liquid tertiary arsines were purified by distillation on a spinning-band column. In the case of the solid tertiary arsines, the pure compounds were obtained from the residue by recrystallization from hot ethanol. Yield data are given in Table I.

General Synthesis of R_3As from the Reactions of R_2Zn and R_3Al with OCH_2CH_2OAsCl. In a 1-L, three-necked, round-bottom flask equipped with a reflux condenser, mechanical stirrer, and pressure-equalizing addition funnel, 0.06 mol of OCH_2CH_2OAsCl was added to 400 mL of *n*-hexane. Then, 0.12 mol of the appropriate alkylating agent in 100 mL of hexane was added slowly with vigorous stirring at room temperature. The reaction mixture was then refluxed for 24 h. After the reaction was cooled to room temperature, any unreacted metal alkyl was hydrolyzed by using 200 mL of a degassed, saturated NH_4Cl solution. The mixture was filtered to remove the solid hydrolysis products. The hexane layer of the filtrate was separated, the three 50-mL hexane extracts of the aqueous layer were combined with the initial hexane layer, and the hexane solution of the arsine was dried over anhydrous Na_2SO_4. After distillation of the hexane, the arsine was distilled on a spinning-band column. Yield data are given in Table I.

The purity of all synthesized arsines was checked by melting point; boiling point; IR spectroscopy; ^1H, ^{13}C, and/or ^{29}Si NMR spectroscopy; and EI mass spectrometry. A satisfactory elemental analysis for $Bu^{sec}{}_3As$ was obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY. Anal. Calcd: C, 58.52; H, 11.05. Found: C, 58.36; H, 11.02.

Supplementary Material Available: Tables of mass spectral data and IR data (2 pages). Ordering information is given on any current masthead page.

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The Hexafluorochlorate(V) Anion, ClF_6^-

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The low-temperature reactions of either $N(CH_3)_4F$ or CsF with ClF_5 in CH_3CN solutions produce white solids, which on the basis of material balances and low-temperature Raman spectra, contain the ClF_6^- anion. The similarity of the Raman spectrum of ClF_6^- to that of the octahedral BrF_6^- ion indicates that ClF_6^- is also octahedral and that the free valence electron pair on chlorine is sterically inactive. The existence of the ClF_6^- anion was further supported by an ^{18}F exchange experiment between ClF_5 and ^{18}F-labeled FNO that showed complete randomization of the ^{18}F isotope among the two molecules. A high-field ^{19}F NMR study of neat ClF_5 and ClF_5 in anhydrous HF solution in the presence and absence of excess CsF has provided accurate measurements of the ClF_5 NMR parameters including, for the first time, both $^{37/35}Cl$ secondary isotopic ^{19}F NMR shifts. Moreover, the NMR study also supports the existence of ClF_6^-, showing that ClF_5 undergoes slow chemical exchange with excess CsF in anhydrous HF at room temperature.

Introduction

The hexafluorohalate(V) anions belong to the interesting class of AX_6E compounds,[2] which possess six X ligands and a free valence electron pair E. Depending on the size of the central atom A, the free valence electron pair E can be either sterically active or inactive. Thus, a recent study has shown that in IF_6^- the free valence electron pair is sterically active, while in BrF_6^- it is not.[3] Whereas the ClF_5 molecule was discovered 27 years ago,[4] and the BrF_6^- and IF_6^- anions have been known for about as long,[5,6]

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the ClF_6^- anion has so far proven elusive. For example, ClF_5 does not form any stable adducts with alkali-metal fluorides and the only reaction observed is a catalytic decomposition of ClF_5 to ClF_3 and F_2.[7] Furthermore, a ^{18}F radiotracer study of the CsF–ClF_5 system did not provide any evidence for fluorine exchange and, thereby, for the formation of a ClF_6^- intermediate.[8] The well-established existence of the ClF_6^+ cation[9-12] and of the $ClF_6^\bullet$ radical,[13] combined with the recent finding that in BrF_6^- the bromine free valence electron pair is sterically inactive,[3] indicated that the weak Lewis acidity of ClF_5 and the low solubilities of CsF and $CsClF_6$ in ClF_5 are the most likely reasons for the previous failures[7,8] to isolate the ClF_6^- anion. Our recent success[14] with handling ClF_3 in CH_3CN solution and the surprisingly high thermal stability of $N(CH_3)_4ClF_4$, combined with its high solubility in CH_3CN, suggested that similar reaction conditions, i.e., the use of $N(CH_3)_4^+$ as a large, stabilizing counterion, of CH_3CN as a solvent, and of low temperature, might provide the long sought after ClF_6^- anion.

Experimental Section

Caution! Mixtures of ClF_5 or ClF_6^- salts with organic materials, such as CH_3CN or $[N(CH_3)_4]^+$ salts, are highly explosive and must be handled on a small scale with appropriate safety precautions, such as barricades, face shields, heavy leather gloves, and protective clothing.

Materials. The CH_3CN (Baker, Bio-analyzed, having a water content of 40 ppm) was treated with P_2O_5 and freshly distilled in a flamed-out Pyrex vacuum system prior to use, thereby reducing its water content to ≤4 ppm. The CsF (KBI) was dried by fusion in a platinum crucible and ground in the drybox. The ClF_5 (Rocketdyne) was purified by fractional condensation prior to its use. The synthesis of HF_2^-- and H_2O-free $N(CH_3)_4F$ is described elsewhere.[15]

Apparatus. All reactions were carried out in well-passivated (with ClF_3) Teflon–FEP or Kel-F ampules that were closed by stainless steel valves. The ClF_5 was handled in a stainless steel–Teflon–FEP vacuum line,[16] and the CH_3CN was transferred on a baked-out Pyrex vacuum line equipped with Teflon stopcocks. Nonvolatile materials were handled in the dry N_2 atmosphere of a glovebox.

Fluorine-18 Exchange Reaction between FNO and ClF_5. A 50-mL nickel can was heated to red heat four times with 2 atm of H_2, followed by pumping each time. The procedure was repeated four times with F_2, followed by treatment with 3 atm of FNO at room temperature for 1 day and pumping for 4 h. Nitric oxide (0.62 mmol) was combined at −196 °C in the can with a Ne/^{18}F-labeled F_2 mixture, which was accelerator produced under conditions previously described.[17] The Ne was pumped off at −196 °C, and F_2 (0.31 mmol) was added to the can. The can was briefly warmed to 20 °C, and the resulting ^{18}F-labeled FNO was condensed, for the removal of any HF, at −196 °C into a U-tube containing 0.5 g of NaF, followed by warming to −78 °C. It was then combined at −196 °C in a $^1/_4$ in. o.d. Teflon–FEP ampule with ClF_5 (0.62 mmol). The resulting mixture was warmed to 20 °C for several minutes and then vacuum-distilled through two U-traps kept at −120 and −196 °C. The −120 °C trap contained the ClF_5, and the −196 °C one, the FNO. Individual activity measurements were corrected for the elapsed time by correcing to zero time of the experiment. At the end of the experiment, the −120 °C trap, containing ClF_5, showed a zero time activity of 71.6 mCi (84.9%), whereas that in the −196 °C trap, containing the FNO, was 12.7 mCi (15.1%).

Synthesis of $N(CH_3)_4ClF_6$. In a typical experiment, $N(CH_3)_4F$ (150.9 mg, 1.62 mmol) was transferred in the drybox into a prepassivated Teflon–FEP ampule that was closed by a stainless steel valve. Dry CH_3CN (5.96 mL, 4.702 g) was added at −196 °C on the Pyrex vacuum line, and the mixture was warmed to room temperature. ClF_5 (1.62 mmol) was added at −196 °C on the stainless steel vacuum line, and the mixture was kept at −31 °C for 3 h with occasional very careful agitation. All material volatile at −31 °C was pumped off and trapped in a −196 °C trap and consisted of 4.70 g of CH_3CN. The white solid residue was highly shock sensitive and consistently exploded when either exposed to a laser beam at low temperature or warmed to room temperature.

When the above experiment was repeated at room temperature, gas evolution set in at about 0 °C, and after solvent removal at 20 °C, a stable white solid was obtained, which, on the basis of its weight and vibrational spectrum, was identified as $N(CH_3)_4ClF_4$.[14]

When CsF was substituted for $N(CH_3)_4F$ in the reaction with ClF_5 in CH_3CN at −31 °C, the volatile materials at −31 °C consisted of the CH_3CN and ClF_5 starting materials, and the nonvolatile residue was unreacted CsF.

For the recording of the low-temperature Raman spectrum of $CsClF_6$, a solution of ClF_5 in CH_3CN was kept in contact with excess CsF for several hours at −40 °C and then slowly cooled to −110 °C. The Raman spectrum of the product in the bottom of the tube was recorded at −110 °C and indicated the presence of $CsClF_6$ (see below) and solid CH_3CN.

Nuclear Magnetic Resonance Spectroscopy. The ^{19}F NMR spectra were recorded unlocked (field drift < 0.1 Hz h^{-1}) by using a Bruker WM-250 or AM-500 spectrometer equipped with a 5.8719 or 11.744 T cryomagnet, respectively. On both instruments, spectra were obtained by using 5-mm combination $^1H/^{19}F$ probes operating at 235.361 MHz (WM-250) or 470.599 MHz (AM-500).

The 5.8719-T ^{19}F spectra were typically accumulated in a 16K memory. Spectral width settings of 5 and 10 kHz were employed, yielding data point resolutions of 0.62 and 1.22 Hz and acquisition times of 1.638 and 0.819 s, respectively. No relaxation delays were applied. The number of free-induction decays accumulated was typically between 2000 and 10000 transients.

The 11.744-T ^{19}F spectra were accumulated in a 16K memory. Spectral width settings of 5 and 30 kHz were employed, yielding data point resolutions of 0.61 and 3.59 Hz and acquisition times of 1.638 and 0.278 s, respectively. No relaxation delays were applied. Typically 80–1000 transients were accumulated.

On both instruments the pulse width corresponding to a bulk magnetization tip angle, θ, of approximately 90° was equal to 1 μs. No line-broadening parameters were applied in the exponential multiplication of the free-induction decays prior to Fourier transformation.

The spectra were referenced to neat $CFCl_3$. The chemical shift convention used is that a positive (negative) sign signifies a chemical shift to high (low) frequency of the reference compound.

Low-temperature studies were carried out by using Bruker temperature controllers. The temperature was measured with a copper–constantan thermocouple inserted directly into the sample region of the probe and was considered accurate to ±1 °C.

Fluorine-19 NMR samples were prepared in 25-cm lengths of AWG 9 (ca. 4-mm o.d., 0.8-mm wall) FEP plastic tubing heat sealed at one end with the open end flared (45° SAE) and joined, by means of a compression fitting, to a Kel-F valve. The assembly was seasoned overnight with ca. 1 atm of F_2 gas, evacuated, and weighed. A weighed amount of CsF was transferred into a sample tube in a drybox. Both ClF_5 and HF were distilled into NMR tubes through a metal line fitted with a pressure transducer that had been previously seasoned overnight with ca. 1 atm of ClF_5 vapor. The ClF_5 pressure was measured (±0.5% accuracy) in a calibrated portion of the metal vacuum line with a pressure transducer (0–1000 Torr range), whose wetted surfaces were Inconel, and condensed at −196 °C into the FEP NMR sample tube. The amount of HF solvent used was determined by direct weighing of the tube assembly. The FEP tube was heat sealed under dynamic vacuum with its contents frozen at −196 °C. The FEP sample tubes were placed in 5-mm thin-walled precision NMR tubes (Wilmad) in order to run their spectra.

Raman Spectroscopy. Low-temperature Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 488-nm exciting line of an Ar ion laser.

Results and Discussion

Synthesis of ClF_6^- Salts. It was found that the activation energy for the ClF_5–CH_3CN reaction is sufficiently high to permit the judicious handling of ClF_5 in a large excess of dry CH_3CN. Although ClF_5 is a more powerful oxidizer than ClF_3, its pseudooctahedral structure with five fluorine ligands and one free valence electron pair renders it less reactive than the pseudotrigonal-bipyramidal ClF_3.

To take advantage of the high activation energy of the ClF_5–CH_3CN reaction, $N(CH_3)_4F$ was carefully combined with ClF_5 in this solvent at −31 °C. Removal of the solvent at −31 °C resulted in a white, highly sensitive solid that violently exploded

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either on exposure to a laser beam at low temperature or on warming to room temperature, thereby preventing its direct identification. It was shown, however, by quantitative material balances that most of the ClF_5 starting material had been retained by the $N(CH_3)_4F$ at −31 °C.

When the reaction between $N(CH_3)_4F$ and ClF_5 was carried out at temperatures above −31 °C, gas evolution was observed at about 0 °C and, after solvent removal at 20 °C, a stable, white solid was isolated, which was identified by vibrational spectroscopy as $N(CH_3)_4ClF_4$.[14] Since the latter compound is stable up to 100 °C and is not shock sensitive,[14] the explosive material from the −31 °C reaction could not have been $N(CH_3)_4ClF_4$ but most likely was $N(CH_3)_4ClF_6$.

To overcome the experimental difficulties associated with the characterization of $N(CH_3)_4ClF_6$, the $N(CH_3)_4F$ starting material in the $N(CH_3)_4F$–ClF_5–CH_3CN system was substituted by CsF. It was hoped that $CsClF_6$ would be stable at −31 °C, the lowest temperature at which the CH_3CN solvent could be pumped off at a reasonable rate. However, it was found that $CsClF_6$ is thermally unstable even at −31 °C, and all the ClF_5 was pumped off at −31 °C, together with the CH_3CN solvent. Since CH_3CN is a much weaker Raman scatterer than the chlorine fluorides,[14] it was possible to record the low-temperature Raman spectrum of $CsClF_6$ without removal of the CH_3CN and, thereby, to identify the ClF_6^- anion. A detailed discussion of the observed spectrum will be given below.

^{18}F Radiotracer Study. Further evidence for the formation of the ClF_6^- anion was obtained by an ^{18}F radiotracer study of the ClF_5–^{18}FNO system. It was found that ClF_5 undergoes rapid fluorine exchange with ^{18}FNO (eq 1). Within several minutes

$$^{18}FNO + ClF_5 \rightleftharpoons [NO^+ClF_5{}^{18}F^-] \rightleftharpoons FNO + ClF_4{}^{18}F \qquad (1)$$

at room temperature, complete randomization of the ^{18}F isotope had occurred. The measured values of 84.9% for the radioactivity in ClF_5 and 15.1% in FNO are in excellent agreement with the values 83.3 and 16.7% predicted for a random distribution of ^{18}F involving an unstable $NO^+ClF_6^-$ intermediate. The rapid fluorine exchange in the FNO–ClF_5 system is in marked contrast to the results from the previous study of the CsF–ClF_5 system for which no evidence of exchange was reported.[8] The lack of exchange in the CsF–ClF_5 system is probably due to the very low solubility of CsF in ClF_5 and not to the lack of ClF_6^- formation (see below).

^{19}F NMR Study of Chemical Exchange Behavior between F^- and ClF_5. Chlorine pentafluoride has previously been shown in two ^{19}F NMR studies to possess a square-pyramidal (C_{4v}) AX_4E structure in the liquid state[19,20] as predicted by the VSEPR model.[2] Alexandre and Rigny[20] demonstrated that, unlike the equatorial X_4 part of the ^{19}F NMR spectrum, which showed a secondary isotopic shift arising from ^{19}F bonded to ^{35}Cl and ^{37}Cl, the axial A part of the spectrum was broadened significantly and showed no evidence for an isotopic shift.[20] This study concluded that chemical exchange between the axial (F_{ax}) and equatorial (F_{eq}) fluorines could be disregarded and that the line broadening of F_{ax} arises from partially quadrupole-collapsed scalar couplings between $^{19}F_{ax}$ and the spin-$^3/_2$ quadrupolar nuclei ^{35}Cl and ^{37}Cl, $^1J(^{19}F_{ax}–^{35/37}Cl)$, which are significantly larger than $^1J(^{19}F_{eq}–^{35/37}Cl)$. Nuclear relaxation time measurements in the same study have confirmed this and have provided estimates of the magnitudes of the scalar couplings ($^1J(^{19}F_{ax}–^{35}Cl)$ = 192 and $^1J(^{19}F_{eq}–^{35}Cl) \leq$ 20 Hz). The larger value for $^1J(F_{ax}–^{35}Cl)$ is in accord with the shorter F_{ax}–Cl bond observed in this molecule.[21] The temperature behavior of the ^{19}F NMR spectrum of liquid ClF_5 was investigated in the previous study, but it does not report any variations of line widths as a function of temperature. We have recorded the ^{19}F NMR spectra of neat ClF_5 at 25, −56, and −90 °C (Figure 1). While there is little effect upon the line width of the F_{eq} resonance on lowering the temperature, a significant narrowing of the F_{ax} resonance line width is observed together with partial resolution of its chlorine isotopic shift. The observed line narrowing for the F_{ax} resonance is attributable to the increased quadrupolar relaxation rates of ^{35}Cl and ^{37}Cl at low temperatures where the isotropic molecular tumbling correlation time (τ_c) for ClF_5 is greater.[22] This behavior is consistent with the dominant contribution of scalar relaxation of the second kind, via $^1J(F_{ax}–^{35/37}Cl)$, to the spin–spin relaxation time (T_2) of the F_{ax} nuclei, as found in the previous study.[20]

The ^{19}F NMR spectra of a solution of ClF_5 (0.536 m) in anhydrous HF and a solution of ClF_5 (0.619 m) in anhydrous HF containing CsF (5.60 m) were investigated. The ^{19}F NMR spectrum of ClF_5 recorded in HF solvent at 25 °C consists of two well-resolved doublets corresponding to equatorial fluorines on ^{35}Cl and ^{37}Cl spin coupled to the axial fluorine environment (Figure 2). The latter environment, as in the neat sample of ClF_5 at 24.4 °C, is broadened significantly owing to partial quadrupole collapse of the $^1J(^{35/37}Cl–^{19}F)$ scalar couplings so that resolution of the isotopically shifted quintets (Figure 2; also cf. Figure 1) is precluded. The line broadening on the quintets is again dominated by scalar coupling and not by fluorine exchange, as has been established for neat ClF_5 in the present and earlier studies.[20] The addition of F^- to HF solutions of ClF_5 results in pronounced broadening of the doublet resonances at 25 °C, preventing resolution of the isotope shift, whereas the appearance of the axial fluorine resonance remains essentially unchanged (Figure 3). The line broadening is consistent with slow intermolecular ^{19}F exchange arising from equilibrium 2 and the intermediacy of ClF_6^- in the

$$ClF_5 + F(HF)_x^- \rightleftharpoons ClF_6^- + xHF \qquad (2)$$

exchange process. Cooling of the ClF_5–F^- sample to −56 °C slowed ^{19}F chemical exchange sufficiently to allow resolution of the equatorial fluorine doublets (Figure 3) and the axial fluorine quintets. This is the first time the two quintet patterns arising from the ^{35}Cl–^{37}Cl secondary isotope effect have been observed in ClF_5. The sharpening of the axial fluorine resonance is not, however, attributed to slowing of the ^{19}F chemical exchange process but is primarily attributed to the dominant effect of the increased quadrupole relaxation rates of the ^{35}Cl and ^{37}Cl nuclei on $^1J(^{35/37}Cl–^{19}F)$ at low temperatures where τ_c for ClF_5 is greater. The addition of CsF presumably increases the viscosity of the solvent medium owing to $F(HF)_x^-$ formation and hence increases τ_c for ClF_5, leading to collapse of the $^1J(^{35/37}Cl–^{19}F)$ couplings. In contrast, the ^{19}F resonances associated with ClF_5 dissolved in HF do not sharpen as significantly, although the quintet pattern clearly possesses a narrower line width than at 25 °C (Figure 2). The broader lines can be attributed to the low viscosity of the HF solvent medium, even at −56 °C, allowing the partially collapsed $^1J(^{35/37}Cl–^{19}F)$ couplings to persist in the slow chemical exchange limit.

The secondary isotope shifts, $^1\Delta^{19}F_{ax}(^{37/35}Cl) = -0.189$ ppm and $^1\Delta^{19}F_{eq}(^{37/35}Cl) = -0.085$ ppm for ClF_5/CsF in HF at −56 °C (Figure 3), follow the usual trend and are negative; i.e., the observed NMR nucleus bonded to the heavier of two isotopes has its NMR resonance to lower frequency.[23] They are comparable in magnitude to those for closely related species in the same row of the periodic table; i.e., for ClF_6^+, $^1\Delta^{19}F(^{37/35}Cl) = -0.15$ ppm,[24] for SF_6, $^1\Delta^{19}F(^{34/32}S) = -0.0552$ ppm,[25] and for SF_4, $^1\Delta^{19}F_{ax}(^{34/32}S) = -0.0690$ ppm and $^1\Delta^{19}F_{eq}(^{34/32}S) = -0.0330$ ppm[25] with the ^{19}F bonded to the heavier isotope occurring at lower frequency. The relative sizes of isotopic shifts are known to be larger for shorter bonds,[26] and this is also true for the secondary isotopic shifts of ClF_5 [$r(Cl–F_{ax}) = 1.58$, $r(Cl–F_{eq}) = 1.67$ Å[21] and $f_{Rax} = 3.01$, $f_{Req} = 2.57$ mdyn Å^{-1}][27] and BrF_5 [$r(Br–F_{ax}) = 1.689$,

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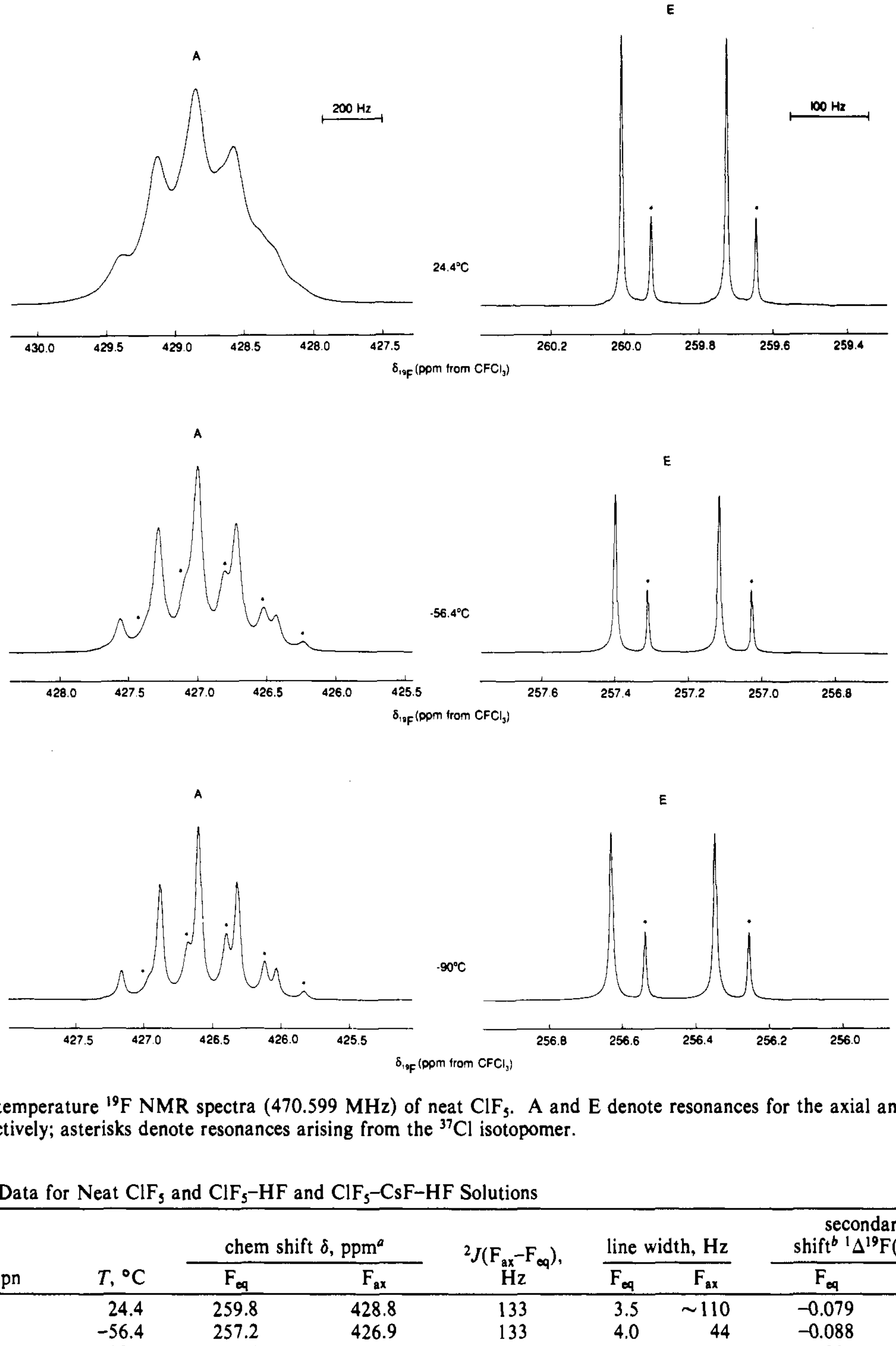

Figure 1. Variable-temperature ^{19}F NMR spectra (470.599 MHz) of neat ClF_5. A and E denote resonances for the axial and equatorial fluorine environments, respectively; asterisks denote resonances arising from the ^{37}Cl isotopomer.

Table I. ^{19}F NMR Data for Neat ClF_5 and ClF_5–HF and ClF_5–CsF–HF Solutions

sample compn	T, °C	chem shift δ, ppm[a]		$^2J(F_{ax}-F_{eq})$, Hz	line width, Hz		secondary isotopic shift[b] $^1\Delta^{19}F(^{37/35}Cl)$, ppm	
		F_{eq}	F_{ax}		F_{eq}	F_{ax}	F_{eq}	F_{ax}
neat ClF_5	24.4	259.8	428.8	133	3.5	~110	–0.079	*e*
	–56.4	257.2	426.9	133	4.0	44	–0.088	–0.1977
	–90.0	256.4	426.6	133	5.2	26	–0.091	–0.199
ClF_5 in HF solv[c]	25	256.4	424.6	130	5.7	~140	–0.078	*e*
	–56.3	253.9	422.6	130	2.5	71	–0.087	*e*
ClF_5/CsF in HF solv[d]	25	253.6	420.9	123	28	~100	*e*	*e*
	–56.3	250.8	418.8	124	6.9	18	–0.085	–0.189

[a] Spectra were referenced with respect to external $CFCl_3$ at 25 °C. [b] $^1\Delta^{19}F(^{37/35}Cl)$/ppm = $\delta(F(^{37}Cl)) - \delta(F(^{35}Cl))$. [c] Concentration of ClF_5 = 0.536 m. [d] Concentration of ClF_5 = 0.619 m, and that of CsF = 5.60 m. [e] Isotopic shift not resolved.

$r(Br-F_{eq}) = 1.774$ Å[28] and $f_{Rax} = 4.07$, $f_{Req} = 3.19$ mdyn Å^{-1}],[27] where $^1\Delta^{19}F_{ax}(^{81/79}Br) = -0.030$ and $^1\Delta^{19}F_{eq}(^{81/79}Br) = -0.015$ ppm.[29] Moreover, the ratio $^1\Delta^{19}F_{ax}(^{37/35}Cl)/^1\Delta^{19}F_{eq}(^{37/35}Cl) = 2.22$ is remarkably similar to those found for the axial and equatorial secondary isotopic shifts of SF_4, $^1\Delta^{19}F_{ax}(^{34/32}S)/^1\Delta^{19}F_{eq}(^{34/32}S) = 2.09$, and BrF_5, $^1\Delta^{19}F_{ax}(^{81/79}Br)/^1\Delta^{19}F_{eq}(^{81/79}Br) = 2.0$.[29] NMR data are summarized in Table I.

Raman Spectrum of $CsClF_6$. The Raman spectrum of the product from the low-temperature reaction of CsF with ClF_5 in CH_3CN solution was recorded at –110 °C in frozen CH_3CN. In the region of the Cl–F fundamental vibrations, three bands were observed at 525, 384, and 289 cm^{-1} (Figure 4, trace A, which, under the influence of the laser beam, rapidly decayed giving rise to new bands at 507, 418, and 290 cm^{-1} (Figure 4, trace B). These new bands are due to the ClF_4^- anion, as shown by the Raman spectrum of $N(CH_3)_4ClF_4$ in CH_3CN recorded under identical

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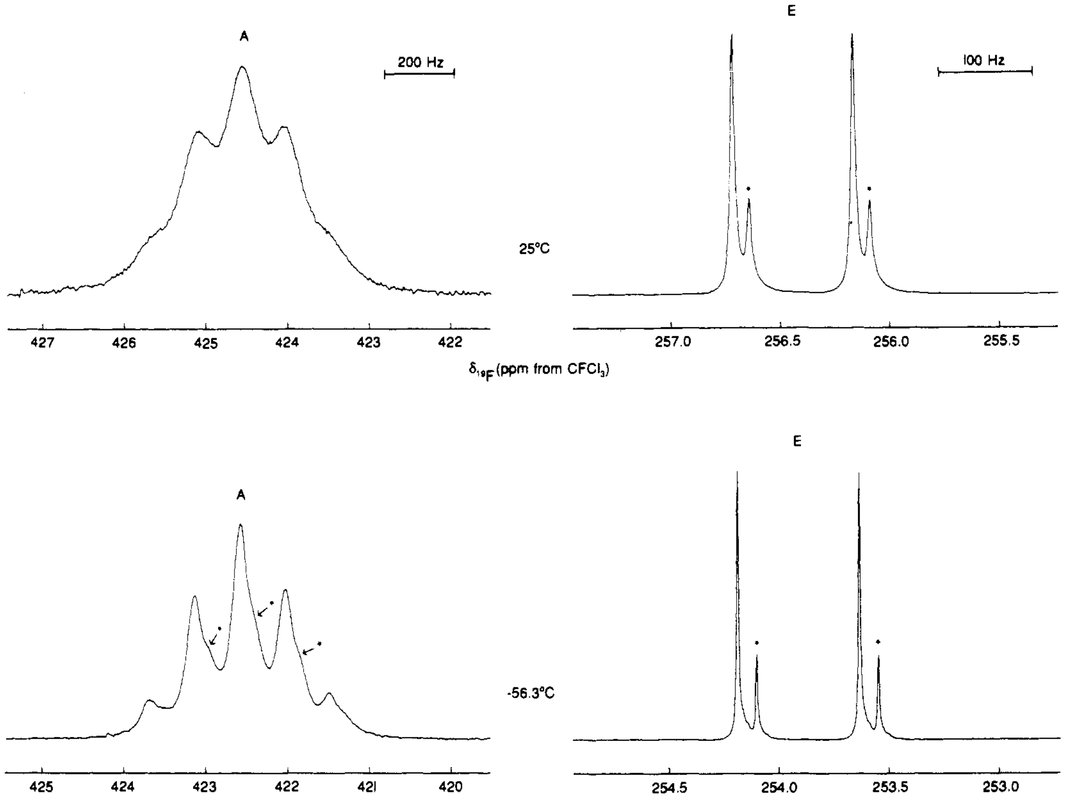

Figure 2. Variable-temperature ^{19}F NMR spectra (235.361 MHz) of ClF_5 (0.536 m) in HF solution. A and E denote resonances for the axial and equatorial fluorine environments, respectively; asterisks denote resonances arising from the ^{37}Cl isotopomer.

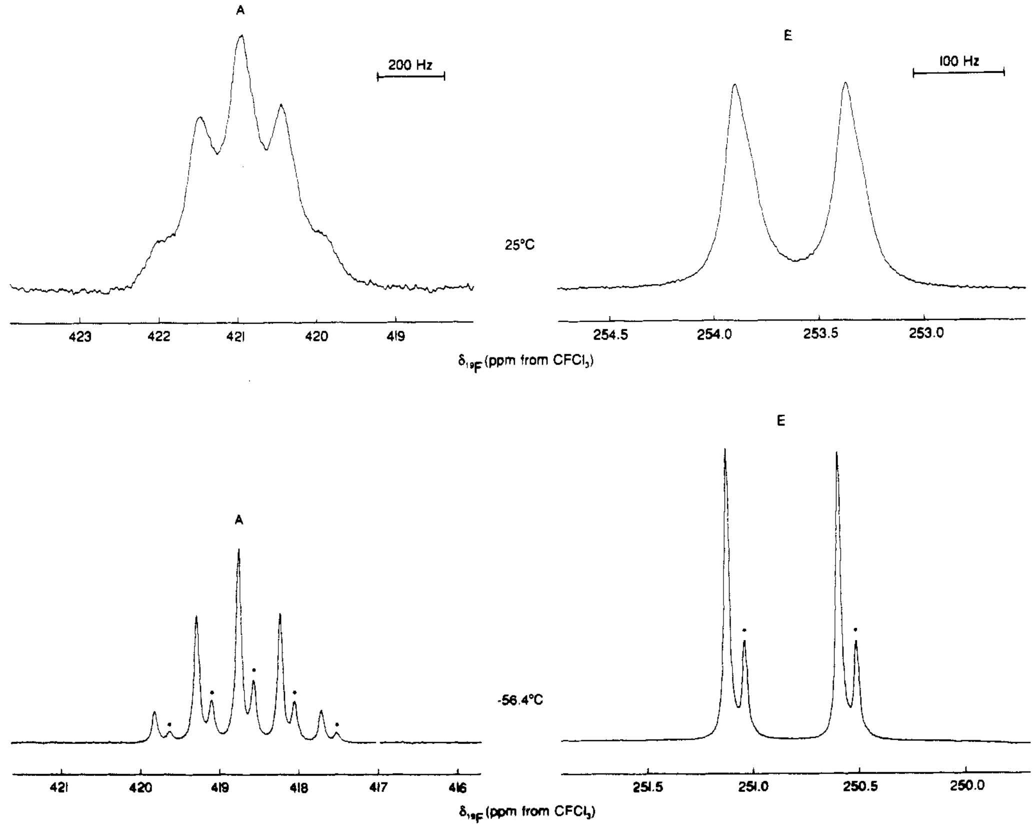

Figure 3. Variable-temperature ^{19}F NMR spectra (235.361 MHz) of ClF_5 (0.619 m)–CsF (5.60 m) in HF solution. A and E denote resonances for the axial and equatorial fluorine environments, respectively; asterisks denote resonances arising from the ^{37}Cl isotopomer.

conditions (Figure 4, trace C). The new set of bands at 525, 384, and 289 cm^{-1} are attributable to ClF_6^- for the following reasons: (i) the bands cannot be assigned to either CH_3CN, ClF_5, or ClF_4^-, (ii) they must be due to a species that on photolysis can produce ClF_4^-, (iii) the relative intensities of these Raman bands are very similar to those observed for solid $Cs^+BrF_6^-$,[18] and (iv) the observed frequencies are in excellent agreement with our expectations for ClF_6^-.

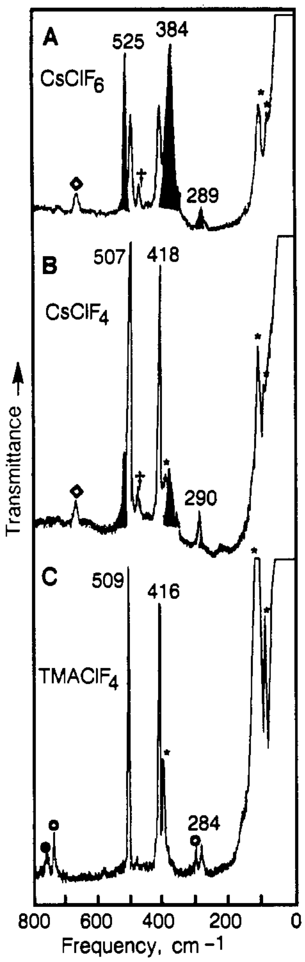

Figure 4. Raman spectra of $CsClF_6$ (trace A), $CsClF_4$ (trace B), and $N(CH_3)_4ClF_4$ (trace C) recorded at −110 °C for the solids in frozen CH_3CN. The bands assigned to the anions of the title compounds are marked by their frequency values. Bands due to ClF_5, CH_3CN, Kel-F, Teflon–FEP, and the $N(CH_3)_4^+$ cation have been marked by daggers, stars, diamonds, hollow circles, and full circles, respectively. Traces A and B are the first and second scan of the same sample and demonstrate the rapid decay of ClF_6^- (solid peaks) to ClF_4^- (hollow peaks) under the influence of the laser beam.

The last point needs some amplification. By analogy with octahedral BrF_6^-,[3] the ClF_6^- anion, which possesses a smaller central atom than BrF_6^-, should also be octahedral; i.e., the free valence electron pair on chlorine should be sterically inactive. Octahedral ClF_6^- should possess six fundamental vibrations of which only the $\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(F_{2g})$ modes would be Raman active. Since in all the Raman active modes the central Cl atom is at rest, the observed frequencies should depend only on the force constants and should be independent of the mass of the central atom. Furthermore, the *F*-matrix expressions of these modes contain the same elements as the corresponding modes of the closely related octahedral $HalF_6^+$ cations and the pseudooctahedral $HalF_5$ molecules and $HalF_4^-$ anions. Therefore, a plot of the frequencies of the modes should be mass independent and should exhibit smooth trends, with the frequencies decreasing with decreasing oxidation state of the central atom and increasing negative charge on the species. Plots of the sums of the frequencies of the symmetric in-phase and symmetric out-of-phase stretching modes and of those of the scissoring deformation mode for the series BrF_4^-,[30] BrF_6^-,[3] BrF_5,[26,31] and BrF_6^+[32,33] and ClF_4^-,[34] ClF_6^-, ClF_5,[21,26,35] and ClF_6^+[36] are shown in Figure 5. With the exception of the ClF_6^- values, all the other frequencies had previously been established experimentally. As can be seen from Figure 5, the frequencies observed in this study for ClF_6^- perfectly fit the expected trends and strongly support their assignment to an octahedral ClF_6^- anion.

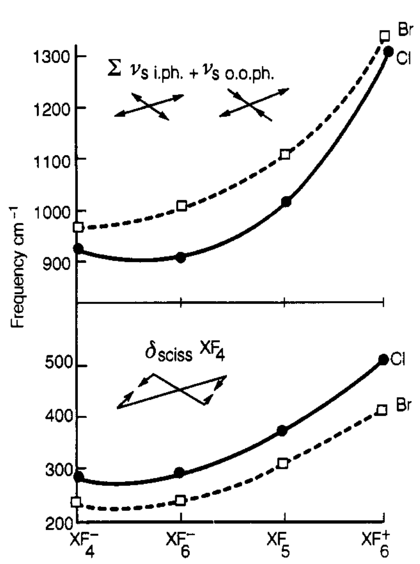

Figure 5. Plots of the sums of the frequencies of the two symmetric stretching modes and of those of the scissoring deformation mode for the different octahedral and pseudooctahedral halogen fluoride ions and molecules. The symmetry coordinates of each mode are depicted by the arrow diagrams.

Conclusion. The results from this study, i.e., Raman spectroscopy and the ^{18}F radiotracer study, provide strong evidence for the existence of the ClF_6^- anion and its octahedral structure. As previously suggested, the past failures[7,8] to isolate the ClF_6^- anion are due to its thermal and photolytic instability, combined with the low solubility of CsF and $CsClF_6$ in liquid ClF_5. These problems were overcome by the use of the larger counterion $N(CH_3)_4^+$, which helps to stabilize the ClF_6^- anion and increases the solubility of the resulting salt, the use of CH_3CN as a more effective solvent, and the use of low-temperature spectroscopic techniques. The obvious limitations of this approach are the horrendous incompatibility problems encountered when one works with one of the most powerful known oxidizers in an organic solvent with an organic counterion. In view of our previous work[3] on the structure of BrF_6^-, the steric inactivity of the free valence electron pair on the chlorine atom of ClF_6^- is not surprising and is at variance with the conclusions reached from a theoretical study, which examined the Laplacian of the calculated electronic charge distribution of gaseous ClF_6^- and predicted a fluxional structure having a distorted octahedral (C_{3v}) equilibrium geometry.[37]

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