Synthesis and Characterisation of Chlorofluoroantimonates(V)

Michael F. A. Dove*,[a] **and Jeremy C. P. Sanders**[b]
[a] *Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK*
[b] *Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1, Canada*

Five of the eight possible chlorofluoroantimonate(V) anions have been characterised in solution by ^{121}Sb and ^{19}F NMR spectroscopy; of these three have been isolated in at least 90% purity as their tetraalkylammonium salts and their infrared and Raman spectra have been assigned. None of the three *trans* isomers was detected either in solution or in the solid state. Factors influencing the appearance of the antimony NMR spectra of the octahedral anions are discussed. The course of the solvolysis of the $SbCl_6^-$ ion by anhydrous HF has been shown to be irreversible and to generate all possible stoichiometries of the chlorofluoro-anions in succession.

There have been several reports concerning the formation of chlorofluoroantimonate(V) anions.[1] The reaction of SbF_5 with chlorides is reported to give $SbClF_5^-$ and a number of its salts with organic cations have been described:[2] nevertheless, a definitive characterisation of this anion was not given. The treatment of $[NR_4][SbF_5(OH)]$ ($R = C_2H_5$ or C_4H_9) and of $[N(C_2H_5)_4][SbF_4(OH)_2]$ with $POCl_3$ had been stated to produce the corresponding monochloro- and dichloro-anions; unfortunately neither anion was properly characterised.[3] The anions $SbCl_4F_2^-$, $SbCl_2F_4^-$ and SbF_6^- were reported to be formed in the reactions between SbF_5 and NaCl in liquid SO_2 at −15 and −45 °C.[4,5] According to Kolditz, X-ray powder diffraction showed that the $SbCl_2F_4^-$ product was not a mixture of the $SbCl_6^-$ and SbF_6^- compounds.[1] On the basis of its infrared spectrum the $SbCl_4F_2^-$ anion was shown to be the *cis* isomer.[5] The action of liquid HF upon $M[SbCl_6]$ (M = Na, K, Rb or Cs) has been shown[6] to generate products with the stoichiometry $M[SbCl_2F_4]$. Ali and Dove[7] found similar behaviour for the salts with $M = N(CH_3)_4$ or $N(C_2H_5)_4$: they also detected a range of related products in the salts obtained from the reactions of $N(C_2H_5)_4Cl$ with $SbCl_4F$, $SbCl_3F_2$ and $SbCl_2F_3$ in liquid SO_2; the products were not just mixtures of the $SbCl_6^-$ and SbF_6^- salts and yet they were not readily separable into pure components.

Our preliminary communication[8] stressed the considerable value of ^{19}F and, more especially, ^{121}Sb NMR spectroscopy in characterising chlorofluoroantimonates(V) ions in solution under conditions of slow fluoride-exchange. This paper describes how suitable synthetic methods were selected, once NMR spectroscopy had been recognised as the analytical technique of choice, to optimise the conditions for preparing substantially pure samples of salts of these anions. Several of the NMR parameters cited in our preliminary publication have had to be revised in the light of subsequent work and analysis and this report presents the best set of data known to us. It must be remembered that Buslaev and co-workers[9] investigated the ^{19}F NMR spectra of mixtures of $SbCl_5$ and SbF_5 in CH_3CN and assigned the numerous broad resonances obtained from the aged and, presumably, partly hydrolysed solutions to a range of chlorofluoro-anions. We have not been able to reproduce their results and as we pointed out earlier it is surprising that the resonance they attributed to SbF_6^- did not show the expected $^1J(^{19}F-^{121}Sb)$ coupling.[10]

Experimental

Reagents.—Anhydrous hydrogen fluoride (ICI, fluorine cell grade) was dried by two distillations *in vacuo* at 0 °C in a fluoroplastic vacuum manifold. Antimony(V) fluoride was prepared by direct fluorination of pure antimony with a mixture of F_2 and N_2 in a flow system, followed by vacuum distillation of the product: antimony(III) fluoride (Aldrich) was resublimed at 285 °C *in vacuo*. Antimony(V) chloride was a BDH product redistilled under reduced pressure; $SbCl_4F$ was prepared by the reaction between $SbCl_5$ and liquid HF[7b] and purified by recrystallisation from a solution in $SbCl_5$. Tetraethylammonium chloride (Fluka) was dried *in vacuo* at 80 °C for 24 h; the tetrafluoroantimonate(III) salt was prepared as described in the literature.[11] Tetraalkylammonium salts of the $SbCl_6^-$ and SbF_6^- anions were prepared from $SbCl_5$ and SbF_5 in solutions of the ionic halide in the corresponding hydrohalogenic acid; the salts were recrystallised from $CHCl_3$ and CH_2Cl_2–CCl_4, respectively. Liquid chlorine (ICI) was dried over phosphorus(V) oxide at room temperature and distilled before use. Acetonitrile (Rathburn Chemical, HPLC grade) was purified by a multistage procedure developed by Winfield,[12] which yields a product suitable for use with reactive moisture-sensitive compounds such as SbF_5 and AsF_5. Adducts of SbF_5 with CH_3CN and C_5H_5N were synthesised by the addition of an excess of the base to the pentafluoride; the excess of base was removed *in vacuo*.

Spectroscopic Measurements.—Infrared spectra were measured on a Philips Analytical SP200 or Perkin Elmer 983G spectrometer over the range 4000–200 cm^{-1}; in general spectra were obtained from thin layers of solutions in CH_3CN or from Nujol mulls between CsI windows. Raman spectra were derived from multiple scans using a Spex Ramalog spectrometer with Scamp data processing and an argon-ion laser giving up to 800 mW at 514.5 nm: samples were studied either as polycrystalline material or as solutions in CH_3CN. The NMR spectra were generated from solutions in CH_3CN contained in 10 mm spinning sample tubes. The spectrometers used were: a JEOL FX90 (2.1139 T) at the City of London Polytechnic, a Bruker WH400 (9.395 T) at Warwick University, using the facilities provided by the SERC and organised by Professor W. McFarlane and Dr. O. Howarth, respectively; a WM250 at Nottingham. Typical acquisition parameters for these studies were as follows: ^{19}F, 400–8000 scans, sweep width 16 kbytes, pulse width 8 μs, 12.2 Hz per point; ^{121}Sb, 12 500 scans, sweep width 16 kbytes, pulse width 18 μs, 6.1 Hz per point; ^{123}Sb, 25 000 scans, sweep width 16 kbytes, pulse width 21 μs, 4.0 Hz per point.

Line-broadening parameters used in the exponential multiplication of the free induction decays were usually set equal to their respective data-point resolutions. Resolution enhancement

Table 1 Products from the solvolysis of $[NR_4][SbCl_6]$ by anhydrous hydrogen fluoride

R	Reaction temperature/ K	Reaction time	Product composition (%)
C_2H_5	298	1.5 h	40 *fac*-Cl_3F_3 60 *cis*-Cl_2F_4
	273	2 h	60 *fac*-Cl_3F_3 40 *cis*-Cl_2F_4
	298	7.25 h	$>$90 *cis*-Cl_2F_4 $<$10 *fac*-Cl_3F_3
	298	4 d	76 *cis*-Cl_2F_4 22 ClF_5 2 F_6
	263	3.5 h	65 *cis*-Cl_2F_4 25 *fac*-Cl_3F_3 19 Cl_6
	248	1.5 h	90 Cl_6 5 *cis*-Cl_4F_2 5 Cl_5F
n-C_4H_9	253	1.5 h	$>$90 *fac*-Cl_3F_3 $<$10 *cis*-Cl_2F_4

was effected by multiplying the free induction decay by a Gaussian function using a line broadening equal to the negative value for the natural linewidth; this procedure was found useful when 'analysing' the spectra of mixtures of species where partially overlapping resonances occurred. Most spectra were obtained unlocked and referenced externally to $CFCl_3$ or $SbCl_6^-$. However, T_1 measurements were made on samples using the pulse sequence (180°–τ–90°) whilst deuterium locked; T_1 values were calculated using routines provided in the spectrometer software. The results are not discussed here but in a later paper.

Solvolysis of $SbCl_6^-$ *Salts in Anhydrous Hydrogen Fluoride.*—Typically the procedure was as follows: an excess of anhydrous hydrogen fluoride (*ca.* 3 cm^3) was condensed *in vacuo* on to solid $[N(C_2H_5)_4][SbCl_6]$ (1.44 g, 3.0 mmol) held at 77 K in a 19 mm Kel-F reaction tube; the mixture was allowed to warm to the appropriate reaction temperature, and the HCl gas released was bled off periodically into a cold trap (77 K), see Table 1: after a suitable reaction time the excess of HF and residual HCl were removed *in vacuo*, leaving a white crystalline solid, which was weighed. The product was subjected either to a recrystallisation or to a reprecipitation stage in glass apparatus; it was essentially unaffected by moist air over several weeks. Since the product usually consisted of a mixture of salts it was characterised by multinuclear NMR spectroscopy, however microanalyses for C, H and N were also performed.

Preparation of $[N(C_2H_5)_4][SbF_5(OCH_3)]$.—Lithium metal (0.161 g, 23 mmol) dissolved in dry methanol (30 cm^3) was added dropwise to a stirred solution of $[N(C_2H_5)_4][SbF_6]$ (7 g, 19.14 mmol) in methanol under a dry nitrogen atmosphere: the solution was then refluxed for 1 h. The precipitated lithium fluoride was removed by vacuum filtration and the filtrate evaporated to dryness *in vacuo*. The sticky white solid (6.11 g) which remained was characterised by its ^{19}F NMR spectrum, AB_4 (δ_A −111, δ_B −122); the ^{121}Sb spectrum revealed only the presence of SbF_6^-, which was also detected in the ^{19}F spectrum.

Reaction of $[N(C_2H_5)_4][SbF_5(OCH_3)]$ *with* CH_3COCl.—This was carried out *in vacuo* at 298 K with an excess (5 cm^3) of CH_3COCl; the salt (0.4 g, 0.001 mmol) dissolved and reacted. After 24 h at room temperature the volatiles were removed *in vacuo* to leave a white solid (0.33 g), which when dissolved in CH_3CN was shown by NMR spectroscopy to consist of 75% $[N(C_2H_5)_4][SbClF_5]$ and 25% $[N(C_2H_5)_4][SbF_6]$.

Reaction of $SbF_5{\cdot}L$ *with* $N(C_2H_5)_4Cl$.—Anhydrous $N(C_2H_5)_4Cl$ (0.17 g, 1.01 mmol) was added with shaking to a solution of $SbF_5{\cdot}NCCH_3$ (0.26 g, 1.01 mmol) in CH_3CN (3 cm^3) at 20 °C; the solvent was then removed *in vacuo* to leave a white crystalline solid, which was dissolved in CH_2Cl_2 and reprecipitated with CCl_4. The ^{121}Sb NMR spectrum was consistent with the presence of 95% chloropentafluoro- and 5% hexafluoro-salts. The conversion of the pyridine adduct into the same mixture of products was effected similarly.

Reaction between $SbCl_4F$ *and* $N(C_2H_5)_4Cl$.—Antimony tetrachloride fluoride (0.57 g, 2.02 mmol) was dissolved in dry CH_3CN (3 cm^3) and $N(C_2H_5)_4Cl$ (0.34 g, 2.05 mmol) in CH_3CN (2 cm^3) was added. The pale yellow mixture of products was isolated *in vacuo* and was reprecipitated from CH_3CN by the addition of diethyl ether. The ^{121}Sb NMR spectrum of the solid dissolved in CH_3CN indicated the presence of $SbCl_6^-$ (40%), $SbCl_5F^-$ (28%), $SbCl_4F_2^-$ (25%) and $SbCl_3F_3^-$ (7%).

Reaction between $[N(C_2H_5)_4][SbF_6]$ *and* $[N(C_2H_5)_4][SbCl_6]$ *in* CH_3CN.—A solution containing an equimolar mixture of the two salts in CH_3CN showed no detectable amounts of the chlorofluoro-anions even after 6 months at 298 K: however, the addition of $SbCl_5$ caused the ^{121}Sb NMR spectrum to change so that after 1 month resonances due to mono-, di- and tri-fluoro-anions were apparent, along with those of the starting materials. The ^{19}F NMR spectrum also was consistent with the formation of *cis*- and *trans*-$SbCl_4F{\cdot}NCCH_3$.

Chlorination of $[N(C_2H_5)_4][SbF_4]$.—Dry chlorine gas was passed through a solution of the antimony(III) salt (2.50 g, 7.6 mmol) in dry CH_2Cl_2 at 243 K until the solution acquired a permanent yellow colour. The volatiles were removed *in vacuo* and the white residue (3.06 g) was dissolved in CH_2Cl_2 and reprecipitated with CCl_4. The product was analysed for C, H and N and the results were consistent with the formula $N(C_2H_5)_4SbCl_2F_4$, however the ^{121}Sb NMR spectrum indicated the presence of $SbCl_3F_3^-$ (14%), $SbCl_2F_4^-$ (55%) and $SbClF_5^-$ (31%).

Chlorination of a Mixture of SbF_3 *and* $N(C_2H_5)_4Cl$.—Resublimed antimony trifluoride (1.63 g, 9.1 mmol) and anhydrous $N(C_2H_5)_4Cl$ (1.51 g, 9.1 mmol) were dissolved in dry CH_2Cl_2 and dry chlorine gas was passed into this solution held at 243 K until the solution acquired a permanent yellow colour. The volatiles were removed *in vacuo* and the white residue (3.68 g) was dissolved in CH_2Cl_2 and $CHCl_3$ added until crystallisation took place. The product was analysed for C, H and N and the results were consistent with the formula $N(C_2H_5)_4SbCl_3F_3$, however the ^{121}Sb NMR spectrum indicated the presence of $SbCl_6^-$ (1%), $SbCl_5F^-$ (5%), $SbCl_4F_2^-$ (26%), $SbCl_3F_3^-$ (60%) and $SbCl_2F_4^-$ (8%).

Results

Pentachloromonofluoroantimonate(V) *Anion.*—This species could not be prepared in a pure state and was invariably formed together with the *cis*-tetrachlorodifluoroantimonate(V) anion, however it was readily identified from the broad but characteristic doublet in the ^{121}Sb NMR spectrum at δ 114.9; see Table 2 for details. It was formed in the low-temperature solvolysis of $[N(C_2H_5)_4][SbCl_6]$ by anhydrous hydrogen fluoride, in the reactions of chlorine with SbF_3 and $N(C_2H_5)_4Cl$ in CH_2Cl_2 at 243 K and of $N(C_2H_5)_4Cl$ and $SbCl_4F$ in CH_3CN, and also in the slow $SbCl_5$-catalysed attack on a mixture of SbF_6^- and $SbCl_6^-$ in CH_3CN.

cis-*Tetrachlorodifluoroantimonate*(V) *Anion.*—This was isolated in an impure state in all reactions in which the mono-

Table 2 Antimony-121 NMR parameters for $SbCl_nF_{6-n}^-$ anions (0.25 ± 0.05 mol dm^{-3} in CH_3CN at 295 K)

Anion	$\delta(^{121}Sb)$/ ppm	$^1J(^{121}Sb-^{19}F)$/ Hz	$\Delta\nu_{\frac{1}{2}}(^{121}Sb)$/ Hz
$SbCl_6^-$	0.0		190
$SbCl_5F^-$	114.9	2017 ± 20	512
cis-$SbCl_4F_2^-$	175.6	2068 ± 20	512
fac-$SbCl_3F_3^-$	187.0	2019 ± 10	383
cis-$SbCl_2F_4^-$	183.8	F_t 2164 ± 10	325
		F_c 1961 ± 10	
$SbClF_5^-$	149.3	F_t 2077 ± 10	230
		F_c 1844 ± 10	
SbF_6^-	86.7	1938 ± 2	40

Table 3 Fluorine-19 NMR parameters observed and calculated[a] for $SbCl_nF_{6-n}^-$ anions (0.25 ± 0.05 mol dm^{-3} in CH_3CN at 295 K)

Anion		$\delta(^{19}F)$ obs.	$\delta(^{19}F)$ calc.	Multiplicity[b]
$SbCl_5F^-$		+25.8	+24.8	sxt
cis-$SbCl_4F_2^-$	F_c	−9.0	−10.5	sxt
trans-$SbCl_4F_2^-$	F_t	—	+18.8	
fac-$SbCl_3F_3^-$	F_c	−45.8	−45.8	sxt
mer-$SbCl_3F_3^-$	F_t	—	−16.5	
	F_c	—	−45.8	
cis-$SbCl_2F_4^-$	F_t	−51	−51.8	sxt and oct
	F_c	−80	−81.1	sxt and oct
trans-$SbCl_2F_4^-$	F_t	—	−51.8	
$SbClF_5^-$	F_t	−87.6	−87.1	sxt and oct
	F_c	−117	−116.4	sxt and oct
SbF_6^-		−122.4	−122.4	sxt and oct

[a] Dean and Evans constants: $C = 35.3$ and $T = 6.0$ ppm. [b] sxt and oct signifies equal-intensity sextet and octet owing to coupling to ^{121}Sb and ^{123}Sb nuclei; sxt signifies partially quadrupole-collapsed sextet/octet pattern.

fluoro-anion was also obtained, see above, and under slightly more forcing solvolytic conditions when it was formed along with the *fac*-trichloro-anion. The tetrachloro ion could be recognised from the triplet in the ^{121}Sb NMR and the ^{19}F spectrum; the latter serves to identify it as the *cis* isomer since the fluorine chemical shift was 30 ppm to low frequency of that expected for the *trans* isomer (see Table 3). The *trans* isomer could not be detected in any of these mixtures; if present, it must have been less than 5% of the *cis* isomer.

fac-*Trichlorotrifluoroantimonate*(V) *Anion*.—This anion was isolated in better than 90% purity from the solvolysis of $[N(n\text{-}C_4H_9)_4][SbCl_6]$ with anhydrous hydrogen fluoride at 253 K. The ^{121}Sb NMR spectrum (Fig. 1) was a 1:3:3:1 quartet, sharper than those of the above two ions although broader than that of $SbCl_6^-$; the ^{19}F NMR spectrum (Fig. 2) revealed only a single environment. This ion was also formed in mixtures obtained from the reactions $SbCl_4F\text{–}Cl^-$, $SbF_4^-\text{–}Cl_2$ and $SbF_3\text{–}Cl^-\text{–}Cl_2$, in which it was a major (60%) component, and gradually in the $SbCl_5$-catalysed attack on a mixture of SbF_6^- and $SbCl_6^-$ in CH_3CN.

cis-*Dichlorotetrafluoroantimonate*(V) *Anion*.—This anion was obtained in better than 90% purity from the solvolysis of $[N(C_2H_5)_4][SbCl_6]$ by anhydrous hydrogen fluoride at 298 K after 7.25 h. It was a major component of the mixture formed by the chlorination of $[N(C_2H_5)_4][SbF_4]$ and a minor component from the $SbF_3\text{–}Cl^-\text{–}Cl_2$ reaction. It was characterised by the binomial 'quintet', actually a triplet of triplets, in the ^{121}Sb NMR spectrum (Fig. 3) and in the ^{19}F spectrum (Fig. 4) by the two equal-area resonances at the positions expected for the *cis* isomer.

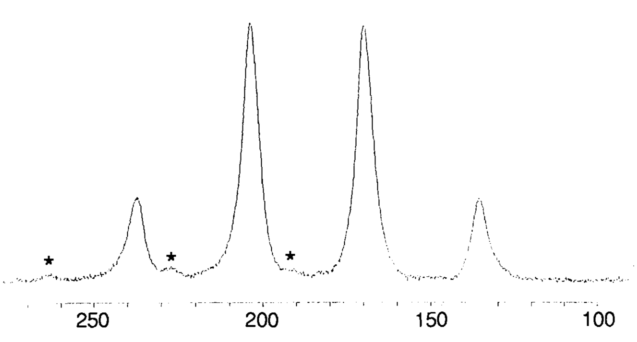

Fig. 1 The ^{121}Sb NMR spectrum (59.859 MHz) of a 0.2 mol dm^{-3} solution of $[N(n\text{-}C_4H_9)_4]$[*fac*-$SbCl_3F_3$] in CH_3CN at 60 °C. Asterisks (*) denote the weak resonances arising from *cis*-$SbCl_2F_4^-$ impurity

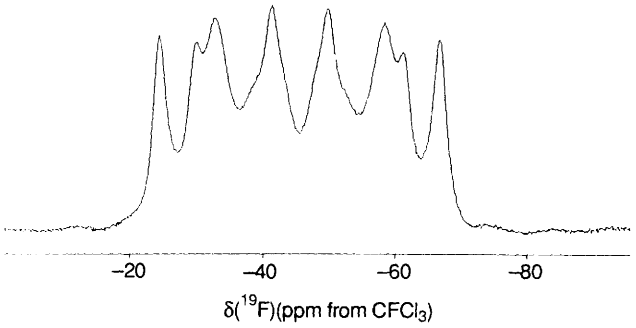

Fig. 2 The ^{19}F NMR spectrum (235.361 MHz) of a 0.2 mol dm^{-3} solution of $[N(n\text{-}C_4H_9)_4]$[*fac*-$SbCl_3F_3$] in CH_3CN at 25 °C

Chloropentafluoroantimonate(V) *Anion*.—This species was first detected among the products of the 4 d solvolysis of $[N(C_2H_5)_4][SbCl_6]$ by anhydrous hydrogen fluoride at 298 K; longer reaction times always led to the formation of increasing amounts of SbF_6^-. The ^{121}Sb NMR spectrum (Fig. 5) is highly characteristic since it clearly shows signs of the two different $^1J(^{121}Sb-^{19}F)$ coupling constants. The ^{19}F NMR spectrum (Fig. 6) is the expected AX_4 pattern with the A component shifted to low frequency of the SbF_6^- resonance; the linewidths of the equatorial (B) fluorines (270 Hz) are narrower than those of the axial (A) fluorine (436 Hz) consistent with the presence of an unresolved two-bond F–F coupling, which is expected to be of the order of 100 Hz. The monochloro-anion was also formed in the chlorination of SbF_4^-, in the reaction of $[N(C_2H_5)_4][SbF_5(OCH_3)]$ with CH_3COCl, and, in >95% purity, in the reaction of $SbF_5 \cdot L$ (L = CH_3CN or C_5H_5N) with $N(C_2H_5)Cl$.

Hexafluoroantimonate(V) *Anion*.—This species contaminated the best $[N(C_2H_5)_4][SbF_5(OCH_3)]$ sample and, hence, the salt of the monochloro-anion prepared from it by the reaction with CH_3COCl. It was also a trace product, readily detected because of the narrow NMR linewidths, after the $SbF_5 \cdot L\text{–}N(C_2H_5)_4Cl$, L = CH_3CN or C_5H_5N, reaction. More interestingly it is clearly the ultimate product of the solvolysis of $SbCl_6^-$ by anhydrous hydrogen fluoride.

Discussion

Antimony-121 *and* -123 *NMR Spectroscopy*.—Despite the favourable receptivities and large chemical shift range, these two nuclei have been little studied.[9,13,14] The main reason is that both possess moderate nuclear quadrupole moments, Table 4, and relaxation is invariably dominated by the efficient quadrupolar mechanism; thus when the antimony nucleus is at a site of low electronic symmetry the resonance can be extremely

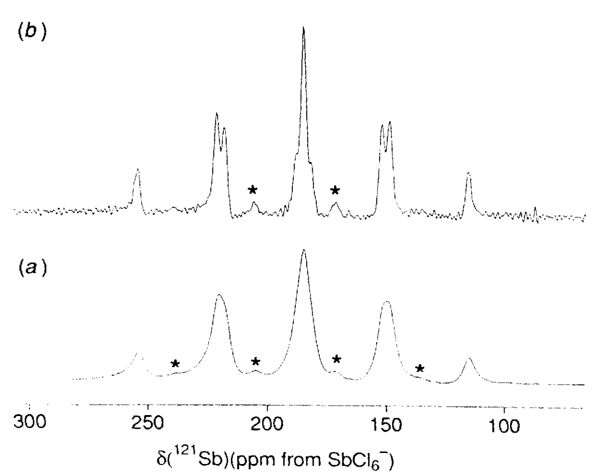

Fig. 3 The ^{121}Sb NMR spectrum (59.859 MHz) of a 0.2 mol dm^{-3} solution of $[N(C_2H_5)_4][$*cis*$\text{-}SbCl_2F_4]$ in CH_3CN at 25 °C: (*a*) normal spectrum; (*b*) resolution-enhanced spectrum revealing the coupling constants $^1J(^{121}Sb\text{-}^{19}F_t)$ and $^1J(^{121}Sb\text{-}^{19}F_c)$ to the two different fluorine ligand environments F_t (F *trans* to F) and F_c (F *trans* to Cl). Asterisks (*) denote the weak resonances arising from *fac*-$SbCl_3F_3^-$ impurity

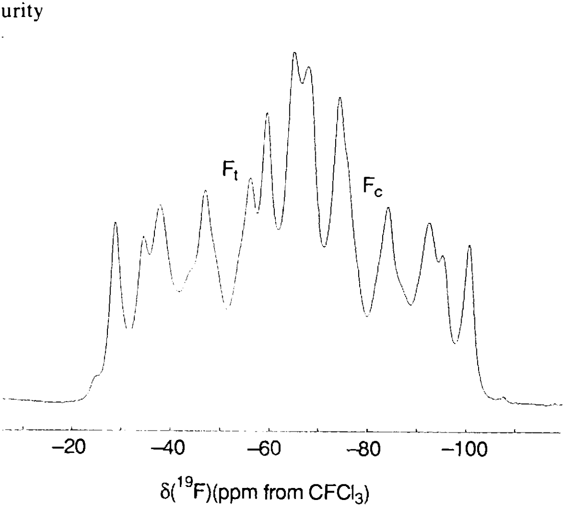

Fig. 4 The ^{19}F NMR spectrum (235.361 MHz) of a 0.2 mol dm^{-3} solution of $[N(C_2H_5)_4][$*cis*$\text{-}SbCl_2F_4]$ in CH_3CN at 25 °C; F_t and F_c represent the centres of the equal-intensity sextet–octet multiplets for the F *trans* to F and F *trans* to Cl environments, respectively

broad. To date, resonances have been observed only for antimony(V) compounds and only for species of high symmetry, *viz*. tetrahedral and octahedral.[15] Although the receptivity of ^{121}Sb is more favourable than that of ^{123}Sb, the linewidth factor $f(I,Q)$ is less favourable by a factor of 2; nevertheless, the larger coupling constant (related to the magnetogyric ratio) for the lighter isotope offsets this and most workers have studied this isotope. The antimony(V) chemical shift range spans, at present, approximately 3500 ppm. The accepted shielding reference is $SbCl_6^-$ in the form of a 0.3 mol dm^{-3} solution of $[N(C_2H_5)_4][SbCl_6]$ in CH_3CN. There have been two studies of the bromochloroantimonate(V) anions, $[SbBr_nCl_{6-n}]^-$; Kidd and Spinney[16] observed seven ^{121}Sb resonances from a 1:1 molar ratio mixture of $[N(C_2H_5)_4][SbBr_6]$ and $[N(C_2H_5)_4][SbCl_6]$ in CH_3CN and assigned them to the seven possible stoichiometries, $n = 0\text{–}6$. Using the pairwise additivity model for the antimony shifts they found very good agreement between the observed and calculated values for all the stoichiometries, including the *cis* ($n = 2$ or 4) and *fac* ($n = 3$) isomers; it was for this reason that they concluded that the *trans* and *mer* isomers were not being detected. Goetz-Grandmont and Leroy[17] obtained broadly similar results but observed two resonances for the $n = 2$ anion which they assigned to the *cis* and *trans* isomers: we note, however, that the assignment to the latter isomer is not in agreement with the calculated shift.

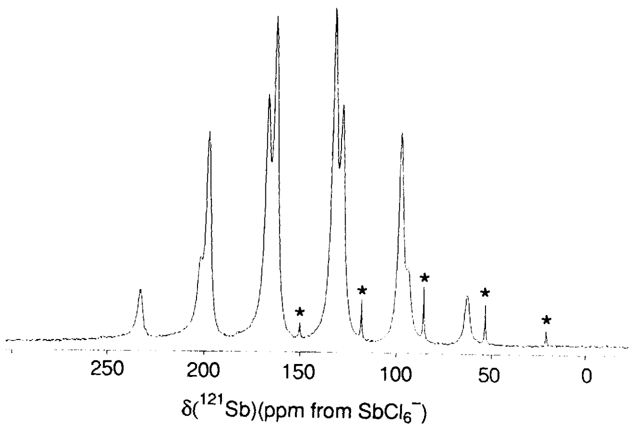

Fig. 5 The ^{121}Sb NMR spectrum (59.859 MHz) of a 0.1 mol dm^{-3} solution of $[N(C_2H_5)_4][SbClF_5]$ in CH_3CN at 25 °C. Asterisks (*) denote the weak resonances arising from SbF_6^- impurity

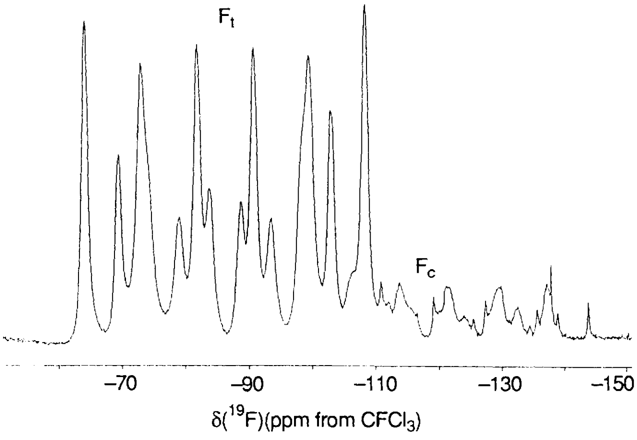

Fig. 6 The ^{19}F NMR spectrum (235.361 MHz) of a 0.1 mol dm^{-3} solution of $[N(C_2H_5)_4][SbClF_5]$ in CH_3CN at 25 °C; F_t and F_c as in Fig. 4

Table 4 NMR characteristics of antimony nuclei

	^{121}Sb	^{123}Sb
Nuclear spin quantum number, I	$\frac{5}{2}$	$\frac{7}{2}$
Natural abundance (%)	57.25	42.75
Magnetogyric ratio/10^7 rad T^{-1} s^{-1}	6.4355	3.4848
Quadrupole moment, $Q/10^{-28}$ m^2	−0.28	−0.36
Resonance frequency/MHz at 2.3488T	24.056	13.026
Linewidth factor*/10^{-54} m^4	2.5×10^{-2}	1.8×10^{-2}
Receptivity relative to ^{13}C	527	113

* Linewidth factor, $f(I,Q) = (2I + 3)Q^2/I^2(2I - 1)$.

Linewidths for the ^{121}Sb and ^{123}Sb resonances of SbF_6^- (0.76 mol dm^{-3} $[N(C_2H_5)_4][SbF_6]$ in CH_3CN at 298 K) were found to be 47 and 37 Hz, respectively; these values agree closely with those calculated from our T_1 data, 46 and 32 Hz. However, an investigation of $SbCl_6^-$ (0.3 mol dm^{-3} in CH_3CN) showed that the observed linewidths, 190 and 108 Hz, are significantly greater than the values, 127 and 88 Hz, from T_1 measurements. This and other evidence for an additional contribution to T_2 resulting from scalar coupling of ^{121,123}Sb to ^{35,37}Cl in $SbCl_6^-$ and also from the analogous coupling to ^{79,81}Br in $SbBr_6^-$ will be presented elsewhere.[18] An important conclusion from that study is that good-quality spectra from either nuclide should be

Table 5 Vibrational spectral data (cm^{-1}) for the anion in $[N(C_2H_5)_4]$-$[SbCl_2F_4]$

Raman		Infrared	
Solution	Solid	(solution)	Assignment
632p	633 (25)	632s	a_1
	589 (1)	602m	b_1 or b_2
563p	565 (20)	565vw	a_1
359p	364 (100)	361mw	a_1
334dp	334 (16)	336mw	b_1
	298 (1)	300 (sh)	
	291 (6)	290m	
	257 (6)	258m	
	223 (8)	224w	
	201 (13)		
	172 (1)		
	148 (17)		
	136 (6)		

Relative intensities in parentheses; s = strong, m = medium, w = weak, sh = shoulder, (d)p = (de)polarised.

obtainable using 0.1–0.5 mol dm^{-3} solutions at 298 K, without excessive use of instrument time. When the stability of the solutions allows then it is an advantage to heat the solutions to, say, 333 K, in order to reduce further linewidths.

The ^{121}Sb NMR spectra obtained in the present study (see Table 2) permitted ready identification of the chlorofluoroantimonate(v) anions present in solution in CH_3CN. The multiplet nature of the resonances arising from the $^1J(^{121}Sb-^{19}F)$ coupling proved to be diagnostic. Effectively the number of fluorines attached to the central Sb controls the number and relative intensity of the transitions. The unequal ^1J couplings in the pentafluoro-anion were clearly evident, whereas in the (*cis*) tetrafluoro-anion they became apparent only after resolution enhancement of the data. The ^{19}F NMR results were essential here to establish that the predominant isomers in solution were always *cis* or *fac*. It invariably proved to be easy to analyse the composition of a mixture of anions by integrating the spectrum in spite of the non-linear dependence of the antimony chemical shifts on the number of bound fluorines. This nonlinearity indicates that the pairwise model using *cis* interactions which has been successful in reproducing the shielding pattern of several octahedral mixed-ligand series, especially $[SbBr_nCl_{6-n}]^-$,[16] $[SnBr_nCl_{6-n}]^{2-}$ [19,20] and $[SnCl_nF_{6-n}]^{2-}$,[19] is inapplicable here. Dillon and Marshall[19] have pointed out that the *cis* Cl–F interaction parameter in the $[SnCl_nF_{6-n}]^{2-}$ series increases with the number of fluorines in the ion: in the present family of chlorofluoroantimonate anions this same parameter actually decreases. Overall the chemical shift trends suggest that the paramagnetic term must be more important than the diamagnetic one in controlling the shifts in this group of ions. A point of interest is the surprisingly small difference between the antimony shifts for SbF_6^- and $SbCl_6^-$, 87 ppm, as compared with those for the analogous ^{31}P and ^{75}As species, 152[21] and 392 ppm.[8] The electronic excitation energy in either antimony or, more likely, arsenic may be responsible for the anomalous paramagnetic shielding term.

Fluorine-19 *NMR Spectroscopy*.—The ^{19}F NMR chemical shifts of the $[SbCl_nF_{6-n}]^-$ family of anions could be calculated satisfactorily (see Table 3) by Dean and Evans'[22] method: the empirical equation is $\delta(^{19}F) = pC + qT$ in which p is the number of Cl substituents *cis* to F (0–4), q is the number of Cl substituents *trans* to F, and C (35.3 ppm) and T (6.0 ppm) are empirical constants. This approach allowed us to calculate the shifts of all possible isomers once the best set of constants C and T had been selected; for our system this was effected using plots of $\delta(^{19}F_t)$ and $\delta(^{19}F_c)$ *versus* the number of fluorine ligands in the ion. The individual resonances in all of the ions appear as an overlapping sextet and octet arising from the two antimony nuclides with spins $\frac{5}{2}$ and $\frac{7}{2}$. This is seen most clearly in the spectrum of SbF_6^- in CH_3CN: the resonances of all the other anions show a broadened, partially collapsed version of this, the broadening increasing progressively from SbF_6^- to $SbCl_5F^-$. The resonances move to higher frequency as the number of chlorine ligands increases; this behaviour is somewhat unexpected since the character of the Sb–F bond is predicted to become more ionic thus giving rise to the reverse trend. The observed tendency is, however, consistent with the effect of the neighbouring dipoles due to the Cl ligands and has been reported for $[SnCl_nF_{6-n}]^{2-}$.[22] Where a given anion contains chemically inequivalent fluorines, *e.g.* F_t and F_c, the resonance of the more ionic F_c always occurs at lower frequency[23] and this was observed in our system. The identification of the isomers with $n = 2$–4 was achieved with the help of their ^{19}F NMR spectra. The trichloro-anion in the most pure specimens (>90%) exhibited only one fluorine environment at δ −45.8 consistent with the calculated value for the *fac* isomer; any *mer* isomer in the solution would be expected to show a resonance at δ −16.5, relative intensity 2 and another at δ −45.8, intensity 1. Both the *cis* and *trans* isomers with $n = 4$ would give rise to single environments, however the calculated chemical shift shows better agreement with that for the *cis* form. There is similarly satisfactory agreement for the ^{19}F resonances of $SbCl_2F_4^-$, confirming the assignment as the *cis* isomer: here it must be remembered that the compound was prepared with well defined stoichiometry, unlike the $n = 2$ species, and also that the ^{121}Sb NMR spectrum shows good evidence for two distinct ^1J couplings.

Vibrational Spectroscopy.—Infrared and Raman data were obtained for the three salts which have been prepared in >90% purity. Results for $[N(C_2H_5)_4][SbClF_5]$, in which the anion is expected to have C_{4v} symmetry, have been assigned very satisfactorily by analogy with the isoelectronic $TeClF_5$.[24] Raman studies of solutions in acetonitrile did not yield reliable polarisation information so data (in italics) were obtained from a polycrystalline solid sample: the infrared spectrum was derived from a solution in acetonitrile. The proposed assignments are as follows (cm^{-1}): (ν_8) 649vs/*644m*, (ν_1 or ν_2) 596mw/*592s* or 560vw/*563w*, (ν_4) 362m/*358s*, (ν_9) 310 (sh), w/-, (ν_3) 290vs/*288w*, (ν_7) -/*273wm*, (ν_{10}) 240m/*238m*, (ν_{11}) -/*154wm*. No bands were detected for the SbF_6^- salt, the principal contaminant detected by NMR spectroscopy.

The spectra of $[N(C_2H_5)_4][SbCl_2F_4]$ were similarly obtained although the polarisation properties of the stronger Raman bands were also determined. The proposed (partial) assignments (see Table 5) are based on the C_{2v} *cis* isomer in view of the several coincidences between the Raman and the infrared spectra. No absorption bands were detected for the $SbCl_3F_3^-$ salt, the principal contaminant detected by NMR spectroscopy.

The spectra of $[N(n\text{-}C_4H_9)_4][SbCl_3F_3]$ were derived from a sample containing less than 10% of the $SbCl_2F_4^-$ salt. In terms of the number of bands observed in the spectrum, assignments for the *fac* isomer are not conclusive although they seem the more likely; thus both infrared and Raman show only two bands in the Sb–Cl stretching region, between 300 and 400 cm^{-1}, which may be assigned to the a_1 and e modes. In the Sb–F stretching region there are two strong infrared bands but apparently three (weak) Raman bands, one of which is close to a band in the spectrum of the $SbCl_2F_4^-$ anion. The vibrational data (cm^{-1}) are: 626s/*622w*(*p*), 600s/*601vw*, -/*561vw*, 362m/*357vs*(*p*), 332ms/*328mw*(*dp*), 291m/-, 264ms/*262w*, 212w/*209w*, -/*171w*, -/*130w*.

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