Multinuclear N.M.R. Spectroscopy of $[NEt_4][SbX_nF_{6-n}]$, X = Br or Cl, and $[NEt_4]$-$[AsCl_nF_{6-n}]$ in Solution in MeCN

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The anions in the title, n = 1—6, have been conclusively characterised in solution by ^{19}F, ^{75}As, and ^{121}Sb n.m.r. spectroscopy and, for n = 1—5, shown to be stable with respect to fluorine redistribution reactions.

Several salts containing halogenofluoroanions of group 5 elements have been isolated; thus $SbX_2F_4^-$, X = Cl[1] or Br,[2] and $SbX_4F_2^-$, X = Cl,[3] have been prepared and assigned *cis* octahedral structures on the basis of vibrational spectroscopy. Furthermore Kolditz and Krause[4] claim to have obtained tetra-alkylammonium salts of $SbClF_5^-$, $AsClF_5^-$, $AsCl_2F_4^-$, and $AsBrF_5^-$. However, it is not clear whether all these anions are kinetically stable with respect to halogen redistribution; the bromochloroantimonates(V) do exchange and are formed from $SbCl_6^-$ and $SbBr_6^-$ in MeCN at 28 °C with a half-life of *ca.* 40 h.[5] Fortunately ^{121}Sb n.m.r. spectroscopy is well suited to determine the stoicheiometry of $SbBr_nCl_{6-n}^-$, n = 0—6,

Table 1. ^{75}As and ^{19}F N.m.r. parameters for $AsCl_nF_{6-n}^-$ anions.

	^{75}As[a]			^{19}F[a] δ,p.p.m.[b]		^{19}F[a]
Ion	δ, p.p.m.[b]	Multiplicity[e]	$^1J(^{75}As-^{19}F)$/Hz	Obs.	[Calc.][g]	Multiplicity[c]
AsF_6^-	0.00	st	932	−64.3	[−64.3]	Qu
$AsClF_5^-$	12.2	q of d	*ax.* 897	F_c −61.1	[−61.1][d]	Qu of q[c]
			eq. 1009	F_t −12.5	[−12.5]	Qu of d[c]
cis-$AsCl_2F_4^-$	−0.3	q	av. 1013	F_c −9.1	[−9.3]	Qu
				F_t 38.2	[39.2]	Qu
trans-$AsCl_2F_4^-$				F_t	[39.2]	
fac-$AsCl_3F_3^-$	−42.4	qu	1259	F_c ~ 42	[42.4]	Qu
mer-$AsCl_3F_3^-$				F_c	[42.4]	
				F_t ~ 89	[91.0]	Qu
cis-$AsCl_4F_2^-$	−102.2	t	985	F_c 96.0	[94.2]	Qu
trans-$AsCl_4F_2^-$				F_t	[142.7]	
$AsCl_5F^-$	−212.4	d	925	F_t 149.7	[145.9]	Qu
$AsCl_6^-$	−391.8	s				

[a] Resonance frequencies at 5.8719 T: ^{75}As, 42.830 MHz; ^{121}Sb, 59.859 MHz; ^{19}F, 235.360 MHz. [b] Reference standards: ^{75}As, Et_4NAsF_6 (0.3 M in MeCN), ext.; ^{121}Sb, Et_4NSbCl_6 (saturated solution in MeCN), ext.; ^{19}F, $CFCl_3$ int. [c] $^2J(F_c-F_t)$ = 103 Hz. [d] F_c = F *trans* to Cl; F_t = F *trans* to F. [e] Key: st, septet; s, singlet; d, doublet; qu, quartet; q, quintet; t, triplet; sx, sextet (all having binomial intensities); Qu, quartet; Sx, Sextet; O, octet (all having non-binomial intensities). [f] Resonances are partially quadrupole-collapsed sextet–octet structures arising from ^{121,123}Sb coupling. [g] T = 3.16, C = 51.76 for As results; T = 5.9, C = 55.65 for Sb results.

Table 2. ^{121}Sb and ^{19}F N.m.r. parameters for $SbCl_nF_{6-n}^-$ anions (see Table 1 for footnotes.)

	^{121}Sb[a]			^{19}F[a] δ, p.p.m.[b]		^{19}F[a]
Ion	δ, p.p.m.[b]	Multiplicity[e]	$^1J(^{121}Sb-^{19}F)$/Hz	Obs.	[Calc.][g]	Multiplicity[e]
SbF_6^-	86.6	st	1938	−121.7	[−121.7]	Sx and O
$SbClF_5^-$	149.3	q of d	*ax.* 1859	F_c ~ −120	[−115.8]	Sx and O
			eq. 2088	F_t −85.2	[−86.1]	Sx and O
cis-$SbCl_2F_4^-$	183.9	q	av. 2083	F_c −80.2	[−80.2]	Sx and O
				F_t −50.4	[−50.4]	Sx and O
trans-$SbCl_2F_4^-$				F_t	[−50.4]	
fac-$SbCl_3F_3^-$	187.5	qu	1980	F_c ~ −47	[−44.5]	Sx[f]
mer-$SbCl_3F_3^-$				F_c	[−44.5]	
				F_t	[−14.8]	
cis-$SbCl_4F_2^-$	174.4	t	1981	F_c ~ −11	[−8.9]	Sx[f]
trans-$SbCl_4F_2^-$				F_t	[+20.9]	Sx[f]
$SbCl_5F^-$	114.9	d	2079	F_c +25.0	[+26.8]	Sx[f]
$SbCl_6^-$	0.0	s				

anions, in solution and provides some evidence for the preferential formation of *cis*- and *fac*-isomers in solution.[5,6]

Fluorine-19 magnetic resonance studies of mixed halogenoantimonates(V)[7] and halogenoarsenates(V)[8] have been reported by Buslaev and co-workers. They did not isolate any compounds; rather they investigated aged solutions of $SbCl_5$/SbF_5 and $LiAsF_6$/$SbCl_5$, respectively, in MeCN, and proposed that a wide range of anionic species coexisted. Separate, broad ^{19}F resonances were detected for many species, even for SbF_6^- and AsF_6^-; this is surprising because the high-resolution spectra of these hexafluoroanions are known to show coupling to the central nucleus.[9]

We have now studied the products obtained by the following reactions (a) $AsF_3/Cl_2/Cl^-$, (b) SbX_6^-/liquid HF, X = Cl or Br, (c) $SbF_3/Br_2/Br^-$, and (d) AsF_5/Br^-, under a variety of conditions. Multinuclear n.m.r. spectroscopy† of these products (as NEt_4^+ salts) in MeCN has provided, for the first time, convincing evidence for the identity of most of the possible mixed halogenofluoroanions of arsenic(V) and antimony(V). Our assignments of the ^{19}F, ^{75}As, and ^{121}Sb n.m.r. spectra of the chlorofluoroanions are summarised in Tables 1 and 2. The results for ^{123}Sb are entirely analogous to those for ^{121}Sb and are, therefore, omitted from the rest of this paper. Those for the chlorofluoroantimonates resemble to some extent Buslaev's ^{19}F spectral assignments; however, those for the corresponding arsenates show no agreement whatsoever.

Our results also show that these ions are relatively stable in MeCN (and in certain other solvents) but not in anhydrous HF. All the fluoroanions exhibit either $^1J(^{121}Sb-F)$ or $^1J(^{75}As-F)$ couplings at 28 °C and *ca.* 0.1M concentration in both the ^{19}F and ^{121}Sb or ^{75}As spectra. The resonance linewidths for $MX_nF_{6-n}^-$ increase as n increases from 0 to 5 (with the possible exception of $SbCl_5F^-$) and also are greater for X = Br than for X = Cl. This behaviour reflects the increase in the quadrupolar relaxation rate of the central

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† ^{19}F: I = 1/2; ^{75}As: I = 3/2, $Q = 0.28 \times 10^{-28}$ m^2;[10] ^{121}Sb: I = 5/2, $Q = -0.28 \times 10^{-28}$ m^2;[10] ^{123}Sb: I = 7/2, $Q = -0.36 \times 10^{-28}$ m^2.[10]

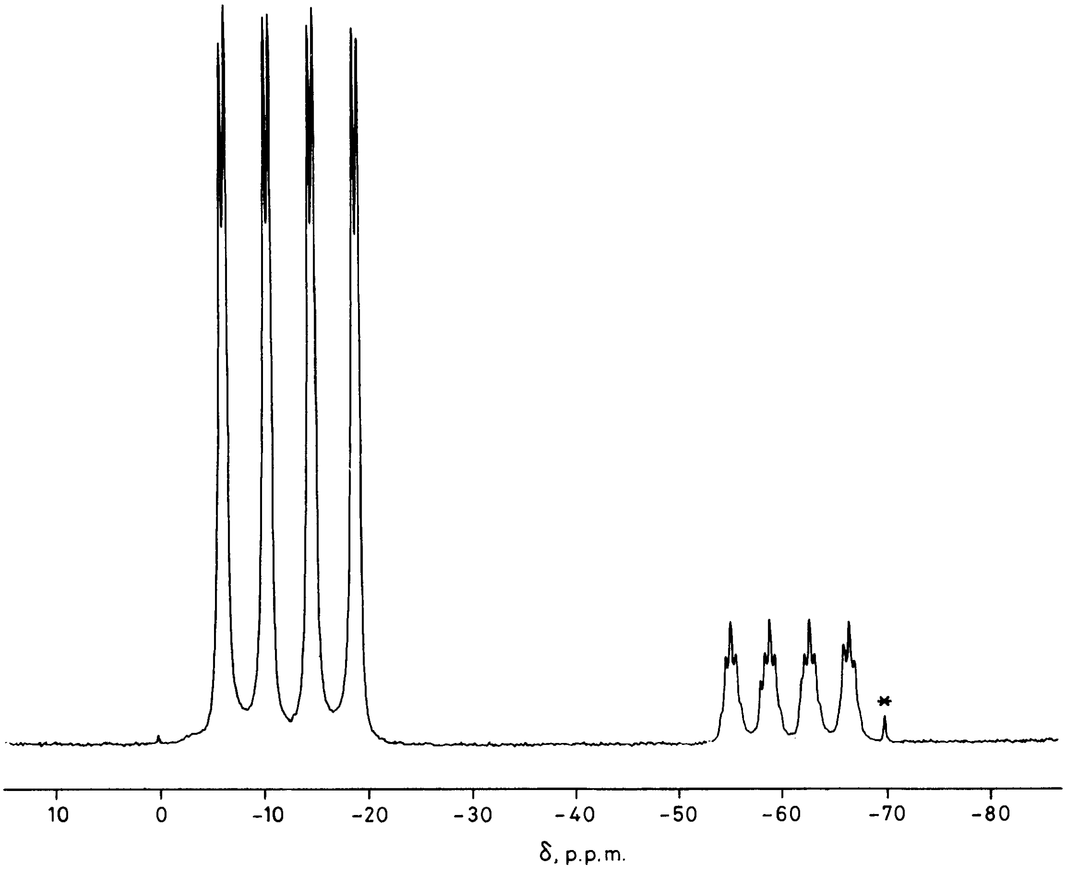

Figure 1. 235 MHz ^{19}F N.m.r. spectrum of NEt_4AsClF_5 in MeCN (*high-field component of AsF_6^- quartet).

nucleus as its octahedral environment is distorted by the replacement of F by the larger halogens. An analogous behaviour has been noted in the bromochloroantimonates(v).[6] However, our systems differ from this in an interesting respect in that the *fac*-trifluoro anions do not give rise to significantly narrower resonances than the other mixed anions.

The linewidths of the two chloropentafluoro anions are sufficiently narrow for the two ^1J couplings (for each species) to be resolved in the ^{75}As and ^{121}Sb spectra; the ^{19}F spectrum of the arsenate, but not the antimonate, shows the ^2J(F–F) coupling (see Figure 1) which leads us to suspect that the quadrupole moment of ^{75}As should be less than that of ^{121}Sb. The reaction of AsF_5 and NEt_4Br in MeCN produces AsF_6^- as well as the first bromofluoroarsenate anion to be characterised satisfactorily, $AsBrF_5^-$ [$\delta_{As} = 102.5$, $\delta_{F(eq)} = 3.81$, $\delta_{F(ax)} =$ *ca.* −60 p.p.m., av. $^1J(^{75}As–^{19}F)$ 1005 Hz].

In the course of our studies we have isolated samples of $MClF_5^-$ (M = As, or Sb), $SbCl_2F_4^-$, and $SbX_3F_3^-$ (X = Cl or Br), as the NEt_4^+ salts, which were at least 70% pure on the basis of n.m.r. spectroscopy as well as elemental analysis. Solutions of these products in MeCN were observed to be stable for at least 1 month. Hence, we deduce that fluorine redistribution reactions are exceedingly slow at ambient temperatures; exchange processes involving the heavier halogens, although not detectable in our n.m.r spectra, do occur with the thermally less stable compounds, especially $AsCl_6^-$ and $SbBr_6^-$. Thus, the ^{75}As resonance of $AsCl_6^-$, reported here for the first time, dwindles in intensity in a MeCN solution containing AsF_6^- and is replaced by the resonances of $AsCl_nF_{6-n}^-$, $n < 5$. Such redistribution reactions probably occur *via* the lower oxidation states of As or Sb since we find that they are inhibited by the addition of excess of halogen.

Further confirmation of our assignments of the ^{19}F resonances (Tables 1 and 2) to individual isomers has been possible because, for each family of anions, they obey the empirical relationship (1) initially proposed by Dean and Evans.[11] The chemical shifts of the central nuclei were found to be only approximately calculable using the pair-wise additivity[12] approach; it was evident that the shifts could not be satisfactorily calculated, using this three-parameter model, for MXF_5^- and *cis*-$MX_2F_4^-$, species in which fluorines occur *trans* to one another (*cf.* ref. 13).

$$\delta(F) = pC + qT \qquad (1)$$

We wish to draw attention to the merit of investigating such species by n.m.r. spectroscopy for two magnetic nuclei in each; this has enabled us to make unambiguous assignments to *cis*- and *fac*-isomers of $MX_2F_4^-$ and $MX_3F_3^-$. Our results show that these isomers are formed in preference to the *trans*- and *mer*-isomers in all three families of complexes studied. Only for $AsCl_3F_3^-$ was there any evidence for the less favoured, *mer*-isomer and, then, at approximately one eighth of the concentration of the *fac*-isomer.

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