

Fluorine-19 Nuclear Magnetic Resonance Investigations of Complexes of Antimony Pentafluoride. I. Complexes with SO₂ClF and Some Related Weak Bases

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Abstract: The ¹⁹F nmr spectra of the following systems have been studied at low temperature: SbF₅-SO₂ClF, SbF₅-SO₂F₂, SbF₅-CH₃SO₂F-SO₂FCl, SbF₅-SOF₂, SbF₅-SOF₂-SO₂ClF, and SbF₅-SO₂-SO₂ClF. It was found that SbF₅ forms the adducts SbF₅·B and (SbF₅)₂B with SO₂ClF, CH₃SO₂F, SOF₂, and SO₂, but no complex formation was observed with SO₂F₂. In all the complexes the ligand is oxygen bonded. The 2:1 complexes contain a fluorine-bridged Sb₂F₁₀ group and the fluorine bridge is *cis* to the donor. It is concluded that the order of basicity toward SbF₅ for the following bases is SbF₅⁻ > CH₃SO₂F > SO₂ > SOF₂ > SO₂FCl > SbF₅ > SO₂F₂.

As part of a continuing study of the chemistry of SbF₅, we have used ¹⁹F nmr to investigate its interaction with a number of very weak bases (SO₂ClF, SO₂F₂, MeSO₂F, SOF₂, and SO₂). The complex SbF₅·SO₂ in which the SO₂ is oxygen bonded is well characterized both in the solid state and in solution.¹ Olah and his coworkers have used SO₂ClF² and SO₂³ as a solvent for the pentafluoride in the production of carbonium ions and Saunders and Hagen⁴ have also used the first solvent for this purpose. The relative Lewis base strengths of the donors are unknown and therefore it was also of interest to obtain a qualitative order for these. The sulfur-oxygen bond orders of these molecules have previously been estimated from vibrational force constants.⁵

The SbF₅-SO₂ClF System. Antimony pentafluoride and SO₂ClF are miscible in all proportions. At room temperature the lines in the ¹⁹F nmr spectra of the solutions are broad, probably as a result of exchange processes, but in the more dilute solutions of the pentafluoride fine structure is observed at temperatures below about -80°.

Figure 1 shows the spectrum of a solution with SbF₅:SO₂ClF = 1.00:2.67, measured at -115°. The three low-field lines A, B, and C are due to fluorine bonded to sulfur; A is the solvent peak. The remaining lines arise from F-on-Sb. The peaks G constitute an AX₄ spectrum and K, L, M, N, O, and P make up a complex spectrum, the most prominent feature of which is the double doublet M.

Table I

Donor, B	Solvent, S	B/S ^a	Temp, °C	Chemical shifts ^b (φ) and coupling constants, J (Hz)											
				SbF ₅ ·B			SbF ₅ ·SbF ₅ ·B ^c								
				Doub- let	Quin- tet	J	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	J _{F₁-F₂}	J _{F₂-F₃}	
F ^{-d}	HF		-60										100	53	
F ^{-e}	SO ₂		-60				131.2	109.1	89.4	109.1	109.1	131.2			
SO ₂ ClF	SO ₂ ClF		-115	105.1	141.8	96	141.6	110.9	~85.2	~130.3	~95.9	~113.4	93	44	
MeSO ₂ F	SO ₂ ClF	0.96/2.69	-110	101.7	131.2	96		~108.9							
SOF ₂	SOF ₂		-100	102.3	138.4	92									
SOF ₂	SO ₂ ClF	0.48/2.88	-115	102.6	138.6	96	141.1	110.7	~83.1	~128.4	~93.2	~114.1	95	49	
SO ₂ ^f	SO ₂		-78	100.9	133.7	100									
SO ₂	SO ₂ ClF	0.58/3.17	-115	102.0	136.6	100	140.2	109.3	~83.8	~127.3	~94.9	~114.8	98	49	

^a SbF₅ = 1.00. ^b If measured relative to the solvent peak, converted to the φ scale for comparison by using δ(SOF₂) = φ + 73.5 ppm or δ(SO₂ClF) = φ + 99.1 ppm. ^c See II for assignments. ^d R. J. Gillespie and K. C. Moss, *J. Chem. Soc., A*, 1170 (1966). ^e As CsSb₂F₁₁: J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, **47**, 1655 (1969). ^f See footnote e; Moore, *et al.*¹ give 105 and 137 ppm.

Results and Discussion

The chemical shifts (relative to external CFCl₃) and spin-spin coupling constants for the various spectra observed in the region of fluorine-on-antimony are given in Table I.

(1) J. W. Moore, H. W. Baird, and H. B. Miller, *J. Amer. Chem. Soc.*, **90**, 1358 (1968).

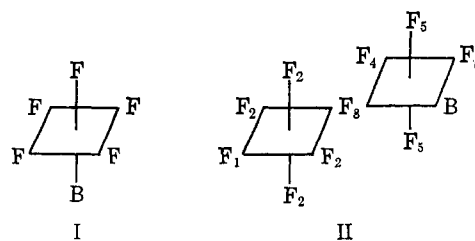
(2) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967); **90**, 933 (1968).

(3) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

(4) M. Saunders and E. L. Hagen, *ibid.*, **90**, 2436 (1968); **90**, 6882 (1968).

(5) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 2074 (1963).

We interpret the spectrum in terms of 1:1 and 2:1 SbF₅:SO₂ClF complexes of the types I and II. The donor is not bound through fluorine and comparison



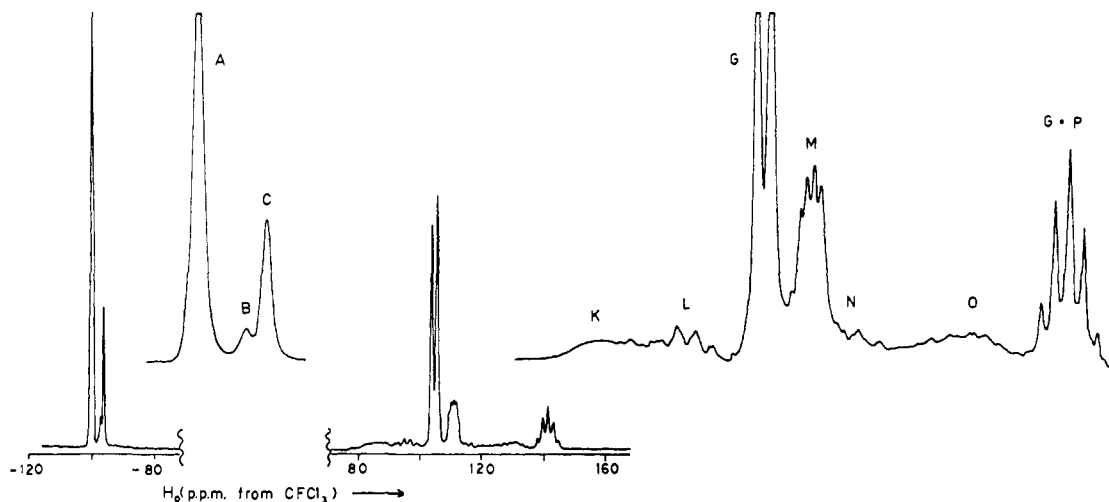


Figure 1. ^{19}F nmr spectrum of a solution with $\text{SbF}_5:\text{SO}_2\text{ClF} = 1.00:2.67$, at -115° .

with the spectra of the MeSO_2F complexes, which are discussed later, indicates bonding through oxygen.

The five fluorines in I will give an AX_4 spectrum as observed for G. The fluorines F_2 in II are expected to be the most intense part of the spectrum of this complex and to be a double doublet from coupling to both F_1 and F_3 and therefore we assign M to F_2 . Double resonance experiments showed that the resonances K and P (under the G quintet) were coupled to M. Comparison of the magnitudes of the coupling constants and the chemical shifts with the known spectrum of the $\text{Sb}_2\text{F}_{11}^-$ anion (Table I) allows us to assign the low-field resonance K to the bridging fluorine F_3 and the resonance P to the terminal fluorine F_1 . If $J_{\text{F}_1-\text{F}_3}$ is near zero as in $\text{Sb}_2\text{F}_{11}^-$,⁶ the resonance due to F_1 will be a quintet by coupling to the four equivalent fluorines F_2 ; under very high resolution a second quintet can be observed under the quintet G (in the corresponding SO_2 complexes (below) the two overlapping quintets G and P can be more easily seen; Figure 4). F_3 will be coupled to fluorines F_2 , F_4 , F_5 , and perhaps F_6 and the multiple splittings can be expected to produce a broad line as seen for K. The structure II is also expected to give three other resonances from F_4 , F_5 , and F_6 (though the spectrum will probably be second order) and three other peaks were observed (L, N, and O). Double resonance showed N coupled to L and O, but apparently not to K; O coupled to K, L, and N; and L coupled to N and O—it was not possible to see whether L was coupled to K. In the similar spectra of the corresponding SOF_2 and SO_2 complexes (below) intensities suggest that L is F_5 , and, since we do not expect F_6 to couple strongly with F_3 , we can tentatively assign O to F_4 , in which case N must be F_6 . Regardless of these tentative assignments the spectrum K, L, M, N, O, and P is in accord with that expected for a complex of structure II.

In the F-on-S region we assign B (+163 Hz from the solvent line) to the fluorine in the SO_2ClF coordinated in II, and C (+228 Hz from the solvent) to that in the chlorofluoride complexed in the 1:1 adduct; the approximate ratio of the intensities $\text{B}:\text{C} = 0.28:1$ is in good agreement with the approximate intensities of the resonances in the F-on-Sb region, which show the mole ratio $\text{II}:\text{I} = 0.30:1$. As expected, B is observed to

(6) See Table I, footnote d.

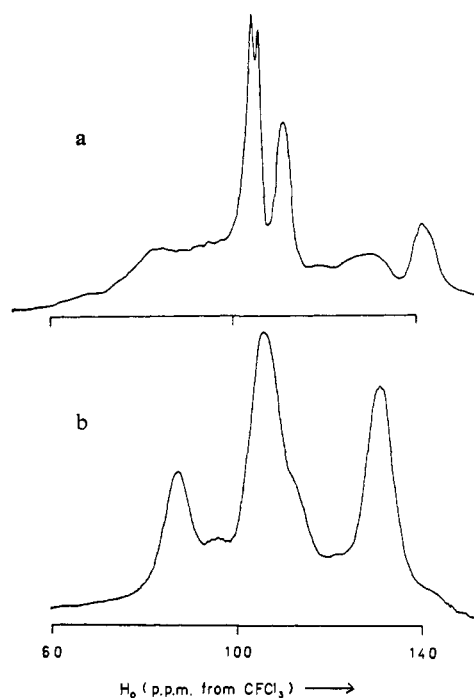


Figure 2. ^{19}F nmr spectra (F-on-Sb region only) of solutions with: (a) $\text{SbF}_5:\text{SO}_2\text{ClF} = 1.00:0.99$, at -110° ; (b) $\text{SbF}_5:\text{SO}_2\text{ClF} = 1.00:0.37$, at -80° .

grow relative to C and A with increasing concentration of SbF_5 in SO_2ClF . At -80° only one average peak is observed in the F-on-S region.

As the concentration of SbF_5 in the chlorofluoride is increased, the solutions become more viscous at low temperatures and there is a corresponding decrease in resolution. However, it can be seen that changes do occur in the spectra of the solutions with increasing concentration (Figure 2). We suggest that these changes correspond to the formation of complexes like II but with more than two fluorine-bridged SbF_5 units. In a solution with $\text{SbF}_5:\text{SO}_2\text{ClF} \approx 1:2$ in the inert (see below) solvent SO_2F_2 , a third line from coordinated SO_2ClF was observed (≈ 120 Hz from the solvent SO_2ClF line), thus lending some support to the postulate of further complexes in more concentrated solutions.

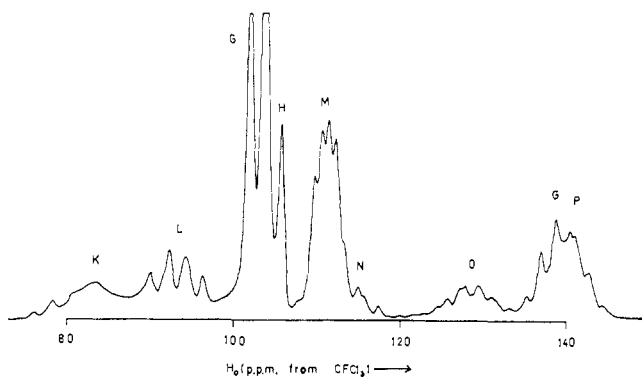


Figure 3. ^{19}F nmr spectrum (F-on-Sb region only) of a solution with $\text{SbF}_5:\text{SO}_2\text{F}_2:\text{SO}_2\text{ClF} = 1.00:0.48:2.88$, at -115° .

Our observations are thus consistent with the formation of a 1:1 complex of type I, a fluorine-bridged 2:1 complex of type II, and possibly other fluorine-bridged complexes with longer SbF_5 chains, in the system $\text{SbF}_5\text{-SO}_2\text{ClF}$. There is no evidence of bonding through fluorine by the SO_2ClF , which we conclude is almost certainly oxygen bonded.

Since both complexes I and II exist in solutions with excess solvent, the Lewis basicity of the type I complex through the *cis* fluorine must be comparable to that of SO_2ClF itself.

The $\text{SbF}_5\text{-SO}_2\text{F}_2$ System. Antimony pentafluoride and SO_2F_2 are miscible at room temperature but on cooling concentrated solutions of SbF_5 a white solid separates from the solution.

When a solution with $\text{SbF}_5:\text{SO}_2\text{F}_2 = 1.00:2.59$ was supercooled to -140° , the ^{19}F nmr spectrum showed only one line in the region of the solvent ($\phi -35.1$) and, in the F-on-Sb region, a spectrum with three peaks ($\phi 81.4, 99.9, \text{ and } 127.9$), which has been shown to be characteristic of polymers of SbF_5 units linked through *cis*-fluorine bridges.⁷ Hence it must be concluded that SO_2F_2 acts as an inert diluent for SbF_5 and that the white solid is the pentafluoride. This implies that an SbF_5 monomer is a better donor (*via* a fluorine bridge) to SbF_5 than SO_2F_2 , a result not unexpected in view of the roughly equal donor properties of $\text{SbF}_5\cdot\text{SO}_2\text{ClF}$ (*via* the fluorine *cis* to SO_2ClF) and SO_2ClF , which is expected to be a better donor than SO_2F_2 .

$\text{SbF}_5\text{-MeSO}_2\text{F}$ Solutions in SO_2ClF . The reaction of SbF_5 with MeSO_2F produces a white solid. Mixtures of SbF_5 and MeSO_2F were of limited solubility in SO_2ClF at the temperatures needed to slow down fluorine exchange, but some results were obtained from supercooled solutions. Measured at -110° , the spectrum of a solution having the composition $\text{SbF}_5:\text{MeSO}_2\text{F}:\text{SO}_2\text{ClF} = 1.00:0.96:2.69$ showed a single line from the solvent, two lines E and F ($+40.3$ and $+42.4$ ppm from the solvent line) of approximate relative intensities 1 and 12, respectively, an AX_4 spectrum, and a complex spectrum of low intensity, the most prominent feature of which was a broadened double doublet. The nmr parameters for the F-on-Sb region are given in Table I.

Since there is only a single line in the region of the solvent, no complexes with coordinated SO_2ClF are present in this solution. The AX_4 spectrum must be

(7) C. J. Hoffman, B. E. Holder, and W. L. Jolly, *J. Phys. Chem.*, **62**, 364 (1958).

given by a 1:1 $\text{SbF}_5:\text{MeSO}_2\text{F}$ complex of type I in which the MeSO_2F is oxygen bonded. Presumably the double doublet is part of the spectrum given by an MeSO_2F complex of type II and we assign it to F_2 . Because of low solubility, it was not possible to obtain spectra from solutions with a greater concentration of dimer.

Variation of the $\text{SbF}_5:\text{MeSO}_2\text{F}$ ratio showed E to arise from free MeSO_2F , and F is assigned to the ligand complexed in the 1:1 complex. No resonance was observed which could be assigned to the MeSO_2F in the type II 2:1 complex; this is expected to be of low intensity and may lie under F. The presence of free solvent in the solution even though $\text{SbF}_5:\text{MeSO}_2\text{F} > 1$ is further evidence for the formation of the dimer in this solution. The resonances from free and coordinated MeSO_2F do not merge until about 25° .

The $\text{SbF}_5\text{-SOF}_2$ System. SbF_5 dissolves in excess thionyl fluoride at room temperature and the ^{19}F nmr spectrum shows broad lines. At lower temperatures fine structure is observed. The spectrum at -100° of a solution with $\text{SbF}_5:\text{SOF}_2 = 1:23$ consists of two peaks in the F-on-S region ($\phi -73.5$ and -46.7) and an AX_4 spectrum in the region of fluorine on antimony (details in Table I). The lines in the F-on-S region merge around -15° . The peak at $\phi -73.5$ is given by the free solvent and the area of the resonance at $\phi -46.7$ is 40% of that of the AX_4 spectrum. The results thus indicate the presence of a 1:1 $\text{SbF}_5:\text{OSF}_2$ complex of type I in this solution. The ligand cannot be fluorine bonded, and a comparison with the spectrum of $\text{SbF}_5\cdot\text{SO}_2$ (in Table I) shows it to be oxygen bonded.¹

It was not possible to obtain spectra from more concentrated solutions of SbF_5 in thionyl fluoride, since crystallization occurred from these at the temperatures required to slow down the fluorine exchange processes. Little evidence was thus obtained for a 2:1 $\text{SbF}_5:\text{SOF}_2$ complex in the pure solvent. The formation of a covalent complex with SOF_2 presents an interesting comparison with the complex $\text{SF}_4\cdot\text{SbF}_5$, which has been shown to be largely ionic ($\text{SF}_3^+\text{SbF}_6^-$) with a small amount of covalent character,^{8a} and with $\text{SOF}_4\cdot\text{SbF}_5$, which has also been shown to have the ionic structure $\text{SOF}_3^+\text{SbF}_6^-$.^{8b}

$\text{SbF}_5\text{-SOF}_2$ Solutions in SO_2ClF . Fine structure was observed in the ^{19}F nmr spectra of $\text{SbF}_5\text{-SOF}_2$ solutions in SO_2ClF at low temperatures (in most cases it was necessary to supercool the solutions). Figure 3 shows the fluorine-on-antimony region of a spectrum obtained from a solution with $\text{SbF}_5:\text{SOF}_2:\text{SO}_2\text{ClF} = 1.00:0.48:2.88$, when supercooled to -115° . Also observed is a peak A from the solvent SO_2ClF and a peak C ($+222$ Hz from the solvent line) in the position expected for $\text{SO}_2\text{-ClF}$ in the $\text{SbF}_5\cdot\text{SO}_2\text{ClF}$ complex (see earlier), as well as two lines E and F (51.8 and 54.1 ppm from the solvent, *i.e.*, $\phi -47.3$ and -45.0) in the region of coordinated SOF_2 (see above). In the spectrum of a freshly cooled solution the relative areas of C, E, and F are 1.0, 4.7, and 3.3.

In the F-on-Sb region the spectrum is complicated but similar to that observed for solutions of SbF_5 in SO_2ClF (Figures 1 and 2 and Table I). It consists of

(8) (a) J. A. Evans and D. A. Long, *J. Chem. Soc.*, **4**, 1688 (1968); M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, submitted for publication; (b) M. Brownstein, P. A. W. Dean, and R. J. Gillespie, *Chem. Commun.*, submitted for publication.

an AX₄ pattern G, partly overlapping a small doublet H which is presumably part of a further AX₄ spectrum, together with the complex spectrum K, L, M, N, O, and P. This latter spectrum is so similar to that assigned to the complex SbF₅·SbF₅·SO₂ClF above that there can be little doubt it is due to a dimer of the type II with B = oxygen-bonded SOF₂. Hence, by comparison we can assign K to F₃, M to F₂, and P to F₁; again it was not possible to make definite assignments for L, N, and O, but the intensity of L appears greater than that of either N or O so that it can be tentatively assigned to F₅, since this is expected to be twice as intense as the resonances of F₄ and F₆. By comparison with the corresponding SO₂ClF complex (see above) it is suggested that O be assigned to F₄, and therefore N to F₆. Both E and F have greater intensity than C and so the larger AX₄ pattern G must be from the 1:1 complex SbF₅·OSF₂, while the small doublet H must be part of the AX₄ spectrum of SbF₅·SO₂ClF.

When the solution was kept at -115°, slow crystallization occurred and the intensity of G decreased relative to M, while the intensity of E decreased relative to F. Thus we can assign E to the SOF₂ complexed in the type I complex and F to that in the type II complex.

We conclude that both the "monomer" and the "dimer" with coordinated SOF₂ occur in solutions in SO₂ClF when the SOF₂:SbF₅ ratio is low. Since both occur to a much larger extent than the complex SbF₅·SO₂ClF even though SO₂ClF is present in excess, both SOF₂ itself and the complex SbF₅·OSF₂ (through the fluorine *cis* to OSF₂) are stronger donors than SO₂ClF.

SbF₅-SO₂ Solutions in SO₂ClF. Dilute solutions of SbF₅ in SO₂ have been shown to contain the type I complex SbF₅·SO₂.¹ We have found this complex to be insoluble in solutions having more than about 20 mol % SbF₅ and there is no evidence of "dimer" formation even in a saturated solution. However solutions with low SO₂:SbF₅ ratios could be prepared using SO₂ClF as solvent; often supercooling was necessary to obtain low-temperature spectra.

At -115° a solution where SbF₅:SO₂:SO₂ClF = 1.00:0.58:3.17 gave the spectrum shown in Figure 4 for the region of F-on-Sb. Again a peak A is observed from the solvent SO₂ClF, together with a weak line C which has a chemical shift (+221 Hz from the solvent) showing it to arise from SO₂ClF complexed in SbF₅·SO₂ClF (see earlier). The features in the F-on-Sb region resemble those of solutions of SbF₅ and SbF₅·SOF₂ in the chlorofluoride. Again we assign the AX₄ spectrum G to the 1:1 complex SbF₅·SO₂ and H to the SbF₅·SO₂ClF complex (the intensity ratio to C is correct). K, L, M, N, O, and P are given by the fluorine-bridged type II complex with B = SO₂ (oxygen bonded); by analogy with the corresponding complexes with SO₂ClF and SOF₂, we can definitely assign K to F₃, M to F₂, and P to F₁, and tentatively assign L to F₅, N to F₆, and O to F₄. Slow crystallization of the supercooled solution causes the intensity of the spectrum of the 1:1 complex to decrease relative to that of the 2:1 complex and allows the correct assignment of the quintets P and G. Since so little SbF₅·SO₂ClF is formed in this solution we conclude that both SO₂ and SbF₅·SO₂ are stronger Lewis bases toward SbF₅ than SO₂ClF.

Measurement of Lewis Basicities. Some relative donor strengths have been determined in the above

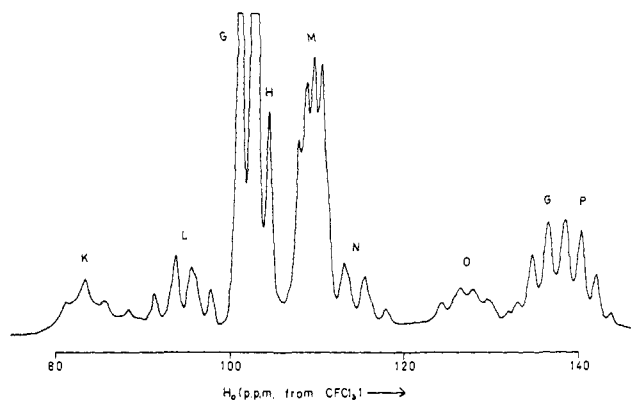


Figure 4. ¹⁹F nmr spectrum (F-on-Sb region only) of a solution with SbF₅:SO₂:SO₂ClF = 1.00:0.58:3.17, at -115°.

systems. To provide a more complete series of basicities, various mixtures of two potential donors were allowed to compete for the SbF₅ in the presence, when necessary, of a relatively inert solvent. Except for the SO₂ClF solutions described above, there was no evidence for the formation of appreciable amounts of the type II complex of one donor in the presence of an excess of another donor; normally only one of the two possible type I complexes or a mixture of the two was formed. The spectra of the various 1:1 complexes are not very sensitive to changes in solvent so that assignments could easily be made, and the observation of separate signals from free and complexed fluorine-containing ligand allowed the amount of complexed ligand to be easily determined. For example, in the low temperature (-100°) spectrum of a solution where SbF₅:SO₂:SOF₂ = 1.00:3.52:5.42, the resonances from the free and coordinated SOF₂ had relative areas 95:5 so that the ratio of complexed SOF₂ to complexed SO₂ = 27:73, indicating SO₂ to be the stronger donor.

The following pairs of potential ligands were allowed to compete for SbF₅ (the first ligand in each pair was found to be the stronger base): SbF₆⁻ (as the Et₄N⁺ salt)-MeSO₂F in SO₂; MeSO₂F-SO₂; SO₂-SOF₂.

Conclusion

Antimony pentafluoride forms 1:1 SbF₅:donor complexes with SO₂ClF, MeSO₂F, and SOF₂, and 2:1 SbF₅:donor complexes with SO₂ClF, MeSO₂F, SOF₂, and SO₂. In all the complexes the ligand is oxygen bonded. The 2:1 complexes are fluorine bridged through the fluorine *cis* to the donor; the structure of the complexes is reminiscent of the *cis*-fluorine-bridged structure of SbF₅ itself,⁷ but is in contrast to that of the 2SbF₅·FSO₃H complex which is fluorosulfate bridged.⁹ The Sb₃F₁₆⁻ anion, a 2:1 complex in which the donor is SbF₆⁻, was recently shown to contain *cis*-fluorine bridges in solution^{10a} although in the salt Br₂⁺Sb₃F₁₆^{-10b} the bridges are *trans*.

Sulfuryl fluoride was found to behave as an inert diluent for SbF₅.

The donors considered were found to have the following base strengths toward SbF₅: SbF₆⁻ > MeSO₂F > SO₂ > SOF₂ > SO₂ClF > SbF₅ > SO₂F₂,

(9) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, **4**, 1641 (1965).

(10) (a) T. Bacon, P. A. W. Dean, and R. T. Gillespie, submitted for publication; (b) A. J. Edwards, G. R. Jones, and R. J. C. Sills, *Chem. Commun.*, 1527 (1968).

$\text{SbF}_5 \cdot \text{SO}_2\text{ClF} \approx \text{SO}_2\text{ClF}$, $\text{SbF}_5 \cdot \text{OSF}_2 > \text{SO}_2\text{ClF}$, and $\text{SbF}_5 \cdot \text{SO}_2 > \text{SO}_2\text{ClF}$. The basicity of an SO_n group might be expected to be closely related to the SO bond order, *i.e.*, to the relative contributions of $\text{S}=\text{O}$ and S^+-O^- . Hall and Robinson¹¹ have shown that there is a linear relationship between the $\text{p}K$ value for an X_2SO_n compound and the stretching frequency of the SO group and Gillespie and Robinson⁵ have shown that the stretching frequency may be used as a measure of the bond order. Hence it is satisfactory to find that with the exception of $\text{CH}_3\text{SO}_2\text{F}$ and SO_2 for which the order is reversed the base strengths of the donors that we have studied with SO_n groups are in the order that would be predicted from the bond orders given by Gillespie and Robinson.⁵

Experimental Section

Nmr Measurements. Fluorine nmr spectra were measured using a Varian DA-60IL spectrometer operating at 56.4 MHz. The 2497-Hz audio modulation side bands forming part of the base-line stabilization circuitry of the instrument usually overlapped part of the center-band spectrum, and the "lock box" was therefore modified to take an external manual oscillator frequency from a Muirhead D-890-A audiofrequency oscillator. Spectra were then measured using the first upper side band in the field sweep unlock mode.

For the homonuclear decoupling experiments, the irradiating frequency was produced by the Muirhead D-890-A oscillator and the swept frequency by a General Radio Co. 1164A frequency synthesizer.

Low-temperature spectra were obtained using a Varian V-4540 temperature controller with the variable temperature probe.

(11) S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964).

Materials. Antimony pentafluoride was obtained from Ozark Mahoning Co. and purified by double distillation in an atmosphere of dry air, using an all-glass apparatus. The purified material was stored in a Teflon bottle in a drybox.

Sulfuryl fluoride (Matheson of Canada Ltd.) and thionyl fluoride (Peninsular Chemresearch Inc.) showed only one line in the ¹⁹F nmr spectrum and were used without further purification. Anhydrous grade sulfur dioxide (Matheson of Canada Ltd.) was stored in a gas bulb over P_2O_5 , and methyl sulfuryl fluoride (Eastman Organic Chemicals) was distilled and stored over molecular sieves.

Sulfuryl chlorofluoride was prepared from potassium fluoro-sulfinate and chlorine according to Seel and Riehl.¹²

The preparation of tetraethylammonium hexafluoroantimonate was reported previously.¹³

Sample Preparation. In a drybox a weighed amount of antimony pentafluoride was transferred to an nmr tube using an all-glass syringe; for the competition reaction with Et_4NSbF_6 , the tube already contained a known amount of the salt. The tubes were closed with detachable tops and attached to a calibrated glass vacuum line. Gases were condensed into the tube from storage bulbs using pressure difference (or, in the case of a single gas, weight) to determine the amount. If only gases were to be added the tubes were then sealed. When one of the components was to be MeSO_2F , the vacuum line and tube were filled with extra dry nitrogen over the frozen gas and the tube was removed from the line. The top was quickly removed, a flow of extra dry nitrogen led into the tube *via* a hypodermic needle, and a known weight of MeSO_2F added from a hypodermic syringe. The top was then replaced and the sample reattached to the vacuum line, evacuated, and sealed.

Acknowledgments. We thank the United States Air Force Office of Scientific Research for financial support of this work. We are grateful to Mr. J. I. A. Thompson for technical assistance with the nmr spectrometer and to Mr. M. Brownstein, who undertook the study of the system $\text{SbF}_5\text{-SOF}_2$.

(12) F. Seel and L. Riehl, *Z. Anorg. Allg. Chem.*, **282**, 293 (1955).

(13) See Table I, footnote *e*.

Fluorine-19 Nuclear Magnetic Resonance Investigations of Complexes of Antimony Pentafluoride. II. The Reactions of Antimony Pentafluoride with Water, Sulfuric Acid, and Fluorosulfuric Acid

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Abstract: It is shown that water reacts with antimony pentafluoride in solution in SO_2 to form the complexes $\text{SbF}_5 \cdot \text{OH}_2$ and $\text{SbF}_5 \cdot \text{OH}_2 \cdot \text{SbF}_5$. These complexes undergo ligand redistribution reactions such as $2\text{SbF}_5 \cdot \text{OH}_2 \rightleftharpoons \text{SbF}_4(\text{OH}_2)_2^+ + \text{SbF}_6^-$. Excess SbF_5 forms $\text{Sb}_2\text{F}_{11}^-$ and $\text{SbF}_5 \cdot \text{SO}_2$. With sulfuric acid, the complexes $\text{SbF}_5 \cdot \text{OSO}(\text{OH})_2$ and $\text{F}_5\text{Sb} \cdot \text{OS}(\text{OH})_2 \cdot \text{SbF}_5$ are formed. Ligand redistribution reactions similar to those proposed for the $\text{SbF}_5\text{-H}_2\text{O}$ system also occur in the $\text{SbF}_5\text{-H}_2\text{SO}_4$ and $\text{SbF}_5\text{-FSO}_3\text{H}$ systems.

In the preceding paper¹ it was shown that methyl sulfuryl fluoride and sulfuryl chlorofluoride form fluorine-bridged 2:1 SbF_5 :donor complexes in which the donor occupies a terminal position. The complex $2\text{SbF}_5 \cdot \text{FSO}_3\text{H}$, however, has been shown to be bridged by two oxygens of the fluorosulfate group, and to be a strong acid of the fluorosulfuric acid solvent system.² Reac-

tion of SbF_5 with SO_3 gives a fluorosulfate-bridged polymer $(\text{SbF}_4\text{SO}_3\text{F})_n$ and not a simple adduct as SO_2 does.³ It is possible that fluorosulfate bridges might possess some special stability in antimony fluoro complexes but it is more probable that the formation of such

(2) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, **4**, 1641 (1965).

(3) R. J. Gillespie and R. A. Rothenbury, *Can. J. Chem.*, **42**, 416 (1964).

(1) P. A. W. Dean and R. J. Gillespie, **91**, 7260 (1969).