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Investigation of the purity of antimony pentafluoride using ^{19}F NMR

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ABSTRACT

Samples of antimony pentafluoride from different syntheses as well as commercial products were investigated by ^{19}F and ^{1}H NMR and compared. HF was identified as impurity and SbF_6^- specie is also present. Their amounts have been correlated through a method based on ^{19}F NMR.

1. Introduction

The Laboratory of Inorganic Materials (LMI-UMR CNRS 6002) is working for 30 years in the field of synthesis and structural characterization of fluorinated materials. Since 2004, our laboratory has created together with the COMURHEX, the Research Common Laboratory (LCR) entitled "Fluorine Chemistry". Comurhex is the European leader producer of uranium hexafluoride (UF_6). This company has a large experience in synthesising molecular fluorine by electrolysis as well as fluorinating inorganic solids. In the framework of the LCR, several main research topics were defined on the basis of the complementary competences from both partners, such as:

- Synthesis of new fluorinated compounds using molecular fluorine and investigation of the reaction mechanisms.
- Enhancement of the uses of fluorine and fluorinated compounds.
- Development of novel synthesis methods.
- Industrial development of fluorinating agents.

As a representative example of the LCR's activities, this paper focuses on the purity of pure antimony pentafluoride (SbF_5) synthetized from different manners, which can potentially be transferred to a large scale production.

Antimony pentafluoride is of primary industrial interest as it is a strong Lewis acid, a powerful oxidizing and a fluorinating agent [1,2]. Up to now, it is one of the largest fluorination reagents used to produce fluorinated compounds [3]. Antimony catalysts enhance the exchange of fluorine for the halogens and permit the substitution to occur [4]. Recently, SbF_5/porous aluminum fluoride (PAF) catalysts were prepared by impregnating $SbCl_5$ into PAF before treating with anhydrous hydrogen fluoride. This novel fluorination reagent and catalyst was successfully used in organic synthesis as a fluorinating reagent together with a fixed bed catalyst for F/Cl exchange [5].

For industrial purpose, it is necessary to estimate the amounts of HF molecules in antimony pentafluoride as it affects the reactivity of SbF_5 towards the fluorination target. Fluoroantimonic acid ($HSbF_6$) may also be present under the form of a mixture of HF and SbF_5 in various ratios [11]. This acid is exceptionally strong and protonates almost every organic compound. Moreover, the fluoroantimonic acid decomposes rapidly and explosively in contact with water and it reacts with most of the solvents. Therefore, the presence of HF in SbF_5 leads in difficulties for its storage and also for its use as a fluorinating agent.

In this present paper, we investigate the purity of SbF_5 issued from different manners rather than describing these different synthesis methods. Indeed the synthesis route and the name of the companies which are commercializing some of the tested products are kept secret, as well as the fluorination method used by

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Comurhex for confidential purpose. Nevertheless a method of synthesis which allows to produce pure SbF_5 at a large scale is described.

2. Experimental

2.1. Synthesis of SbF5 from Sb powder

Antimony pentafluoride can be prepared by either the reaction of antimony trichloride with excess of fluorine gas [6] or the reaction of antimony pentachloride with anhydrous hydrogen fluoride:

$$SbCl_{3(s)} + 7F_{2(g)} \rightarrow SbF_{5(l)} + 3ClF_{3(g)} \tag{1}$$

$$SbCl_{5(s)} + 5HF_{(g)} \rightarrow SbF_{5(l)} + 5HCl_{(g)} \tag{2}$$

Many experiments were carried out under various conditions such as temperature, pressure and reagent materials. Only the most effective and profitable modes of synthesising SbF_5 of high purity at an industrial scale are reported here.

A cylindrical nickel reactor of 1 m length and offering a volume of 3.6 l was used for the reaction. The heating was ensured by a horizontal tubular oven, surrounding the reactor, with a large temperature homogeneous domain of about 60 cm length. The reacting enclosure was slightly angled to allow the liquid SbF_5 formed by the reaction to be collected at the bottom of this enclosure. The SbF_5 was then cooled with an external water flow and stored in a tight PTFE reservoir.

The procedure is the following: 200 g of antimony powder (Aldrich, 99.9%, grading size from 20 to 100 μm) were spread over two nickel trays stacked in the part of the reactor exhibiting a homogeneous temperature. One can notice that the higher the grading size of the antimony powder is, the lower the reactivity of the powder with the fluorine is. A primary vacuum was settled in both the reactor and the reservoir while the reactor was heated up to 160 °C (temperature for the reaction). High purity fluorine gas (Solvay Fluor and Derivate, purity 98–99% (V/V) with HF max. 0.5% (V/V)) was then introduced with a rate of 12 g h^{-1}. The reaction was extremely fast. The reaction with the fluorine was so fast that none increase of the pressure inside the reactor was detected on the manometer during the first 6 h of the fluorination. First no liquid was collected in the reservoir and a spontaneous increase of the temperature (up to 170 °C) was observed indicating a highly exothermic reaction. This observation is characteristic of the formation of solid SbF_3. Thereafter, the pressure started to increase gradually until reaching the atmospheric pressure after 7 h under the constant fluorine gas flow. This last step is relative to the very slow formation of SbF_5. At this stage about 100 ml of liquid SbF_5 was recovered in the reservoir. It corresponds to 85% of the completion. To avoid a pressure increase beyond one atmosphere, several interruptions of the F_2 gas flow were intermittently performed for a duration of 8 h to reach the recovery of the overall expected quantity of SbF_5 (about 118 ml). For this step the temperature of the oven was gradually increased up to 240 °C. The overtaking of this temperature leads to the sublimation of SbF_3 and avoid the risk to block up the exit of the liquid SbF_5 or to solubilize some SbF_3 with the liquid SbF_5 in the reservoir. Nickel or monel reactors are strongly preferred to stainless steel (for temperatures higher than 150 °C), because this last one drives a yellow color of the resulting SbF_5. This coloration is due to some impurities issued from the reactor. Nevertheless, if a stainless steel reactor is used, pure SbF_5 may be recovered by distillation in a nickel or a monel reactor heated at 150 °C. The as-prepared SbF_5 is labelled LMI. This method was adapted by Comurhex and two batches were synthesized, namely Comurhex 1 and Comurhex 2. In addition, two commercial products were investigated and are called Com 1 and Com 2.

As solid SbF_3 is a possible impurity, SbF_3/SbF_5 mixtures were prepared and characterized and SbF_3 was first synthesized.

2.2. Synthesis of SbF_3 from powdered Sb_2O_3

The reaction of Sb_2O_3 oxide with anhydrous HF gas was performed to obtain antimony trifluoride. The interest of this process comes from the higher reactivity of anhydrous HF towards the antimony trioxide Sb_2O_3, especially for Sb_2O_3 of high granulometry.

The same reactor as the one described in Section 2.1 was used for the synthesis. SbF_3 was obtained from the reaction of 200 g of Sb_2O_3 solid powder with gaseous HF at 160 °C. A flow of dried N_2 gas was passed through a liquid HF reservoir carrying diluted HF vapors into the reactor at a constant N_2 flow rate of 20 g h^{-1} during 5 h. The reaction of antimony oxide (Sb_2O_3) with gaseous HF is the following:

$$Sb_2O_3 + 6HF \rightarrow 2SbF_3 + 3H_2O \tag{3}$$

It is interesting to notice that the synthesis of SbF_3 powder can be the first step to produce SbF_5. Thereafter the following reaction using pure fluorine could be performed:

$$SbF_{3(s)} + F_{2(g)} \rightarrow SbF_{5(l)} \tag{4}$$

At the end of the first reacting period, resulting in SbF_3, and prior to the introduction of pure F_2 gas for the SbF_5 production, the atmosphere of the reactor should be neutralized by a strong pure N_2 flow and also pumped out under primary vacuum. The reaction would occur as aforementioned and would easily reach the completion.

2.3. Characterization

Due to its corrosive and hygroscopic characters, SbF_5 violently reacts with water. To avoid that reaction which would damage the samples, NMR experiments were carried out with SbF_5 samples which were introduced in sealed glass tubes, prepared in a glove box under argon atmosphere. NMR experiments were performed with a Bruker Avance spectrometer, with working frequencies of 300.15 and 282.2 MHz for ^1H and ^{19}F, respectively. A static probe operating with tubes of 5 mm diameter was used. A simple sequence (τ-acquisition) was performed with a single $\pi/2$ pulse of 3.5 μs for both ^{19}F and ^1H.

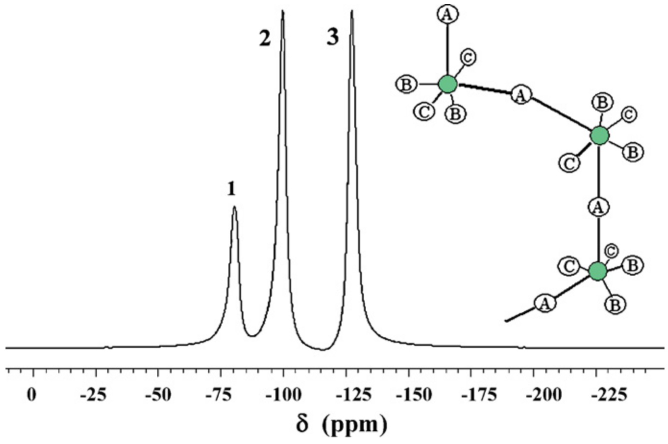

Fig. 1. ^{19}F NMR spectrum of pure SbF_5.

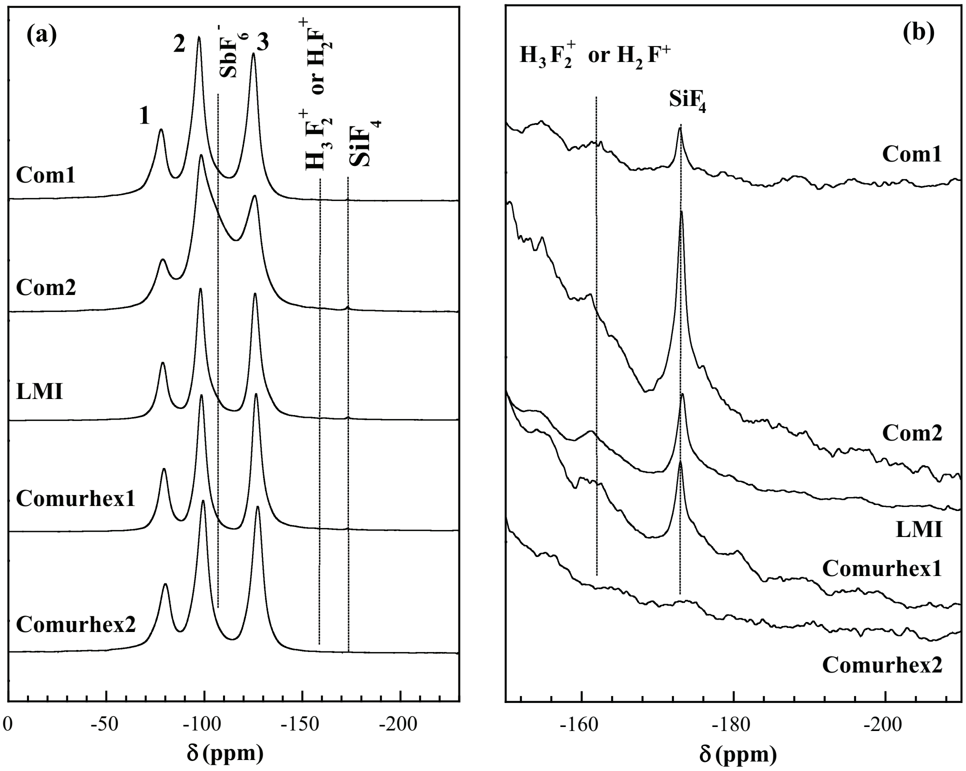

Fig. 2. (a) ^{19}F NMR spectra of SbF_5 from various syntheses; (b) enlargement in the −150/−210 ppm range.

Because one possible impurity is solid SbF_3, a particular attention was devoted to optimize the recycling type D1. As D1 could be large for solid samples, wide D1 range has been covered from 3 to 120 s for each sample. Finally, not any change has been observed and D1 of 3 s has been selected. ^1H chemical shifts are externally referenced to tetramethylsilane (TMS). ^{19}F chemical shifts are given with respect to $CFCl_3$.

3. Purity

In order to investigate the purity of antimony pentafluoride SbF_5, ^{19}F and ^1H NMR experiments were mainly performed as the expected impurities were HF or solid SbF_3. The different NMR spectra recorded are shown in Figs. 1 and 2 for ^{19}F nuclei and in Fig. 3 for ^1H ones.

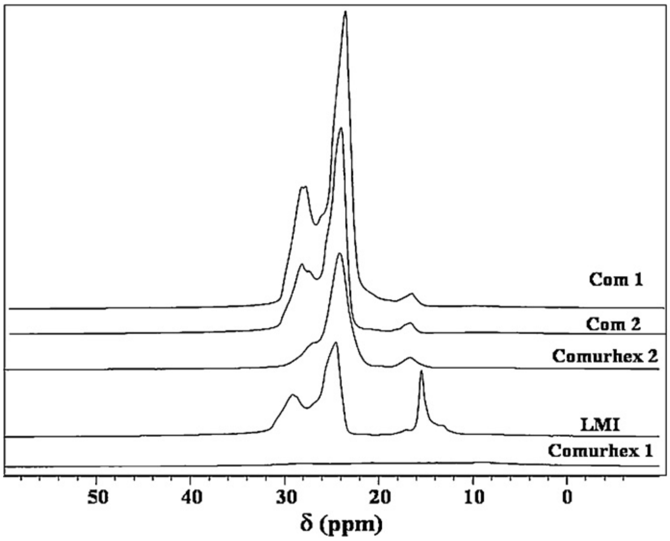

Fig. 3. ^1H NMR spectra of various SbF_5 samples.

In liquid SbF_5, polymerization occurs due to fluoride bridging between Sb atoms (see scheme inserted with Fig. 1). SbF_5 exhibits a ^{19}F NMR spectrum with three lines at −83.7, −102.9 and −130.5 ppm (Fig. 1); the ratios of the integrated intensities are 1/2/2. In accordance with the existence of three groups of ^{19}F nuclei with different neighbouring, labelled A, B and C in Fig. 1 (line 1 is assigned to ^{19}F nuclei A, line 2 and line 3 may be related to either nuclei B or C). The NMR spectrum of pure SbF_5 was fitted with three Lorentzian lines (Fig. 4). An additional fourth Lorentzian contribution was necessary to fit the NMR spectra of some samples presenting a significant HF content. This additional contribution is centered at −110 ppm and corresponds to the chemical shift of SbF_6^- [7,8]. This anion is formed by the reaction of SbF_5 with HF and the other by-products are H_2F^+ and/or $H_3F_2^+$. Such species could be detected by ^1H NMR (Fig. 3).

Chemical equilibria involving SbF_5 are reported in the literature. Self-dissociation is not observed for pure SbF_5 [9,10] and the following equilibria are reported, depending on the molar percentage of SbF_5 in HF:

$$\text{For less than 40 molar \% } SbF_5,\ 3HF + SbF_5 \leftrightarrow H_3F_2^+ + SbF_6^- \quad (5)$$

$$\text{for more than 40 molar \% } SbF_5,\ 2HF + SbF_5 \leftrightarrow H_2F^+ + SbF_6^- \quad (6)$$

Another equilibrium is also reported:

$$2HF + 2SbF_5 \leftrightarrow H_2F^+ + Sb_2F_{11}^- \quad (7)$$

In accordance with equilibrium (6), a good correlation was found between the indirect method using ^{19}F NMR and the intensities of the ^1H NMR lines, as discussed thereafter. Thus, the proportion of SbF_6^- quanlitatively informs about the presence of HF in the samples.

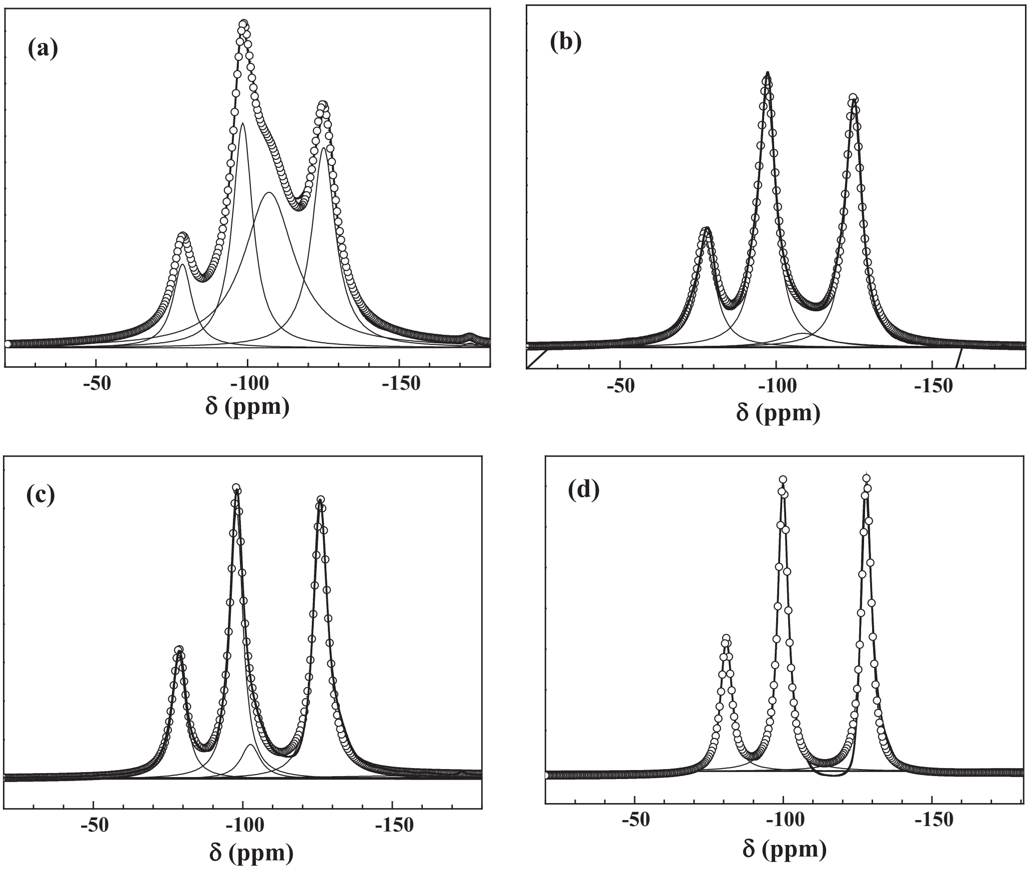

Fig. 4. Fits of the ^{19}F NMR spectra of SbF_5; Com 1 (a), Com 2 (b), LMI (c) and Comurhex 1 (d).

Various samples of SbF_5 were studied by NMR, namely two commercial samples (Com 1 and Com 2), two SbF_5 batches synthesized by Comurhex (Comurhex 1 and Comurhex 2) and one synthesized at the LMI laboratory (LMI). Figs. 2 and 3 show respectively the ^{19}F and ^{1}H NMR spectra for all samples. Fig. 4 displays representative examples of the NMR spectrum fits. From that figure, one can see that the highest purity is found for the sample provided by Comurhex (Comurhex 1) in Fig. 4d and the sample which exhibits the highest content of SbF_6^-, and also HF, is the commercial SbF_5 called Com 1 and presented in Fig. 4a.

According to equilibrium (6), the HF content was indirectly estimated from the amount of SbF_6^- determined from NMR experiments. The HF molar contents and the molar ratios SbF_5/SbF_6^- are summarized in Table 1. The method allows classifying the samples according to their HF content:

Comurhex 1 (~0 molar %) < Comurhex 2 (3.5 molar %) < LMI (7.0 molar %) < Com 2 (9.0 molar %) < Com 1 (43.1 molar %).

SbF_5 samples were studied in sealed glass tubes and HF can react with their walls according to the following reactions:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \qquad (8)$$

and/or

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \qquad (9)$$

The higher the amount of SbF_6^- and also the initial amount of HF is, the higher the formation of gaseous SiF_4 (or H_2SiF_6) is.

The enlargement in the −150/−210 ppm range (Fig. 2b) highlights both the formation of SiF_4 and the low amounts of $H_nF_m^+$.

The HF contents estimated from the fits of NMR data are in good agreement with the classification obtained from ^{1}H NMR (Fig. 3).

It is worth noting that not any trace of SbF_3 have been detected even with experimental conditions for solid state NMR, i.e. longer recycling times, optimized pulse powers and durations. In order to

Table 1
Data extracted from the fittings of ^{19}F NMR spectra for SbF_5 from different ways of syntheses.

Product	S_1 integrated area line 1 at −83.7 ppm	S_2 integrated area line 2 at −102.9 ppm	S_3 integrated area line 3 at −130.7 ppm	S_4 integrated area line of SbF_6^- at − 110 ppm	$n(SbF_5)$[*]	$n(SbF_6^-)$[**]	$n(SbF_5)/n(SbF_6^-)$	$n(HF)$[***]	% molar HF
Com 2	1894	4090	3597	601	1916.2	100,1	19.1	200.2	9.0
Com 1	1505	4304	4483	7542	2058.4	1257	1.6	2514	43.1
Comurhex 2	2148	4101	4107	229	2071.2	38.2	54.2	76.4	3.5
Comurhex 1	2104	4241	4603	0.3	2189.6	0	–	0	0
LMI	1109	2408	2580	287	1219.4	47,8	25.4	95.6	7.0

[*] $n(SbF_5) = (S_1 + S_2 + S_3)/5$.
[**] $n(SbF_6^-) = S_4/6$.
[***] $n(HF) = 2n(SbF_6^-)$.

investigate the effect of the presence of SbF_3 on the measurements, intentional pollution of SbF_5 was carried out. First of all, pure SbF_3 was synthetized as expressed in Section 2.2.

The ^{19}F NMR spectrum of the resulting SbF_3 sample (not shown) exhibits a broad line, centered at −40 ppm. The linewidth can be explained by the nature of the sample (solid), in particular because of strong ^{19}F–^{19}F homonuclear dipolar coupling, and by the NMR spectrum recording conditions (static without magic angle spinning). The chemical shift of SbF_3 given in NMR databases is +24 ppm/$CFCl_3$.

Two SbF_5 (Comurhex 1)/SbF_3 mixtures were prepared under argon atmosphere in a glove box.

- SbF_5 with 2.8 weight percent (wt%) of SbF_3
- SbF_5 with 1.2 wt% SbF_3

The mixtures were introduced into glass tubes (preliminary dried under vacuum at 180 °C overnight to eliminate any moisture traces) and then sealed.

The 3 lines of the SbF_5 NMR spectrum exhibit a shoulder located at about 5 ppm of the centre of the main line (Fig. 5); the chemical shifts of the shoulders are −88, −108 and −136 ppm, when adding SbF_3. Moreover, the intensities of these shoulders are related to the amount of SbF_3. The 1/2/2 intensities ratio of the NMR spectrum of SbF_5 is conserved and such a ratio also appears for the 3 additional shoulders. All these information clearly indicate that the SbF_5 line changes result from the presence of Sb(III). Similarly to SbF_5, Sb centres are linked by bridging fluorides in solid SbF_3. The tendency to form polymeric species is common to SbF_5 and SbF_3. Such polymeric species involving Sb(V) and Sb(III) centres may be formed through bridging fluorides. The nature of this SbF_5–SbF_3 interaction still remains to be clarified (bridging fluorides or dipolar interaction), but ^{19}F NMR thus appears as a qualitative detection method of SbF_3 (with amount of about 1 wt%) taking into account the experimental shifts resulting from the presence of Sb(III).

4. Conclusion

Difference in reactivity of antimony pentafluoride with various precursors for fluorination could be related to the presence of HF molecules. We describe a method using ^{19}F NMR in order to estimate the amount of HF. By comparing several samples issued from different syntheses methods as well as commercial products, we have underlined that the initial amount of HF and the SbF_6^- content in SbF_5 are correlated. SbF_6^- can be detected by the presence on the ^{19}F spectrum of an additional single line. Fits of the spectra allow the amounts of SbF_6^- and then HF to be estimated. Moreover, the presence of Sb(III) centres can also be indirectly detected using ^{19}F NMR taking into account the shift of the 3 lines of SbF_5 because of the presence of Sb(III) centres.

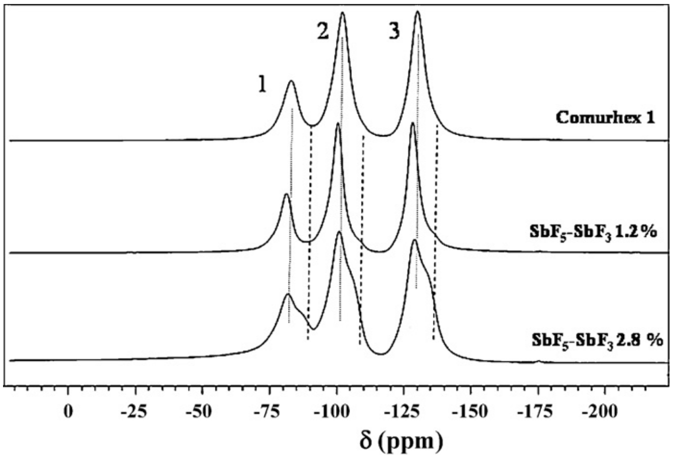

Fig. 5. ^{19}F NMR spectra of SbF_3/SbF_5 (Comurhex 1) mixtures.

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