121Sb MÖSSBAUER SPECTROSCOPY OF ANTIMONY (V) CHLORO FLUORIDES SbCl5-xFx

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Abstract. — 121Sb Mossbauer spectra of a number of compounds of the series SbCl$_5$-xF$_x$ have been measured. The variations of isomer shift and quadrupole coupling are discussed in terms of the molecular geometry.

1. Introduction. — Antimony (V) chlorofluorides have been of much interest as Lewis acid catalysts and as halogenating agents since the early work of Swarts [1]. Often the antimony chlorofluoride used in such studies was just the appropriate mixture of SbCl$_5$ and SbF$_5$, or SbF$_3$ and SbCl$_5$, and little attempt was made to identify the active compound. The pentachloride and pentfluoride are well known, though there is some dispute as to the structure of SbCl$_5$ at low temperatures [2-4]. Crystallographic evidence has shown that both SbF$_5$ [5] and SbCl$_5$F [6] are cyclic tetramers while two other antimony chlorofluorides [7, 8] are claimed to be ionic and contain the [SbCl$_4$]$^+$ cation.

We have now recorded the 121Sb Mossbauer spectra of a number of these compounds. The isomer shifts and quadrupole coupling constants are discussed in terms of the known and most likely structures. Two of the compounds namely SbCl$_4$F$_{1.5}$ and SbCl$_5$F$_3$ give spectra which clearly show the presence of two different antimony sites (Table and Fig. 1).

2. Experimental. — Mossbauer spectra were recorded on apparatus previously described [9]. The source was 0.5 mCi. Ba$^{121m}$Sn(Sb)O$_3$, obtained from New England Nuclear, which was maintained at room temperature while the samples were cooled to liquid He temperature. A Xe-CO$_2$ proportional counter was used to detect the $\gamma$-rays and the window of the single channel analyzer was set on the escape peak of the 37 keV $\gamma$-ray. The samples contained 10 mg Sb cm$^{-2}$ and all isomer shifts were measured with respect to InSb at liquid He temperatures. Each spectrum was calibrated by means of a He-Ne laser interferometer system and periodically checked against a standard iron foil. About 80,000 counts per folded channel were accumulated and spectra were fitted by the procedures already described using the usual fitting procedure [10] and in addition the programme described by Shenoy et al [11] which uses a fast transmission integral routine developed by Cranshaw [12]. Preparative procedures for the compounds studied will be published elsewhere.

3. Results and Discussion. — The results obtained from an analysis of the 121Sb Mossbauer spectra of these compounds are given in the Table. Of the compounds studied the best characterised is SbF$_5$. This is polymeric in the liquid form and X-ray crystallography has shown it to be tetrameric in the solid state [5]. Each antimony has a distorted octahedral arrangement of fluorine atoms, four terminal and two bridging. The large positive isomer shift is the result of the electronegative fluorines removing s electron density from the antimony: $\delta r/r$ is negative for 121Sb. Presumably the quadrupole coupling arises because all fluorines about each antimony are not equivalent and therefore produce an asymmetric electronic charge distribution, nor are the F-Sb-F angles 90° [5]. It should be pointed out however that the spectrum fitted almost as well to a single Lorentzian line.

Two of the compounds namely SbCl$_4$F$_{1.5}$ and SbCl$_5$F$_3$ give spectra which clearly show the presence of two different antimony sites (Table and Fig. 1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>L. S. (*)</th>
<th>$\varepsilon^2 gQ_\delta$</th>
<th>$\Gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbCl$_5$</td>
<td>5.2</td>
<td>-5.7</td>
<td>2.3</td>
</tr>
<tr>
<td>SbCl$_4$F$_x$</td>
<td>6.3</td>
<td>11.8 ($\eta = 0.7$)</td>
<td>3.6</td>
</tr>
<tr>
<td>Sb$<em>3$Cl$</em>{11}$F$_4$</td>
<td>5.3</td>
<td>8.9</td>
<td>2.6</td>
</tr>
<tr>
<td>SbCl$_5$F$_3$</td>
<td>7.7</td>
<td>2.7</td>
<td>3.9</td>
</tr>
<tr>
<td>SbCl$_5$F$_2$</td>
<td>6.8</td>
<td>9.8 ($\eta = 0.8$)</td>
<td>3.8</td>
</tr>
<tr>
<td>Sb$<em>3$Cl$</em>{11}$F$_3$</td>
<td>4.4</td>
<td>3.2</td>
<td>2.0</td>
</tr>
<tr>
<td>SbCl$_5$F$_3$</td>
<td>8.7</td>
<td>13.1</td>
<td>4.0</td>
</tr>
<tr>
<td>Sb$<em>3$Cl$</em>{11}$F$_{11}$</td>
<td>4.4</td>
<td>0</td>
<td>3.1</td>
</tr>
<tr>
<td>Sb$_5$F$_5$</td>
<td>10.1</td>
<td>14.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Sb$_5$F$_5$</td>
<td>10.3</td>
<td>8.7</td>
<td>2.2</td>
</tr>
</tbody>
</table>

(*) The isomer shifts (L. S.) were measured at liquid helium temperatures and refer to InSb at the same temperature.
mony site in \( [\text{Sb}_2\text{F}_1] \) would be more symmetrical than in \( [\text{Sb}_2\text{Cl}_2\text{F}_3] \) but this is not the case. The relatively large coupling indicates that there is a similar Sb-F-Sb interaction between cation and anion in \( [\text{SbCl}_4^+] \) \( [\text{Sb}_2\text{F}_1] \). Unfortunately the positional parameters were unavailable for this compound \( [7] \), not allowing us to confirm this suggestion.

Identification of the \( [\text{SbCl}_4^+] \) species throws some light on the controversial question as to the nature of \( \text{SbCl}_3 \) at low temperature. Ohlberg \( [2] \) has shown that \( \text{SbCl}_3 \) has a trigonal bipyramidal structure at 243 K. At very low temperatures however there appears to be some dispute and various suggestions have been put forward \( [3,4] \). Our Mössbauer data \( [13] \) (and Table) at liquid helium temperatures are certainly consistent with the structure proposed by Ohlberg \( [2] \) since we consistently obtain a negative quadrupole coupling interaction. Furthermore the experimental spectrum can not be fitted to the two antimony resonances expected if it were to be formulated as \( [\text{SbCl}_4^+] \) \( [\text{Sb}_2\text{Cl}_2\text{F}_3] \).

Both \( \text{SbCl}_4^+ \) and \( \text{SbCl}_3\text{F}_3 \) show one site spectra with significant distortions from symmetrical environments. The spectrum of \( \text{SbCl}_4^+ \) is shown in figure 2.

Both compounds have a narrow resonance at low velocity 4.4 mm/s, implying a very symmetrical environment for one site, and a much broader resonance at more positive velocity for the other site. Preliminary X-ray data for \( \text{Sb}_3\text{Cl}_4\text{F}_{11} \) has been interpreted in terms of the ionic salt \( [\text{SbCl}_4^+] [\text{Sb}_2\text{F}_1] \) \( [7] \) and Preiss \( [8] \) has published a more refined structure for \( \text{SbCl}_2\text{F}_3 \) which is formulated as \( [\text{SbCl}_4^+] [\text{SbCl}_2\text{F}_3^-] \). The narrow Mössbauer resonance at 4.4 mm/s, present in both compounds, is assigned to a \( [\text{SbCl}_4^+] \) cation. The \( [\text{Sb}_2\text{F}_{11}]^- \) anion has an isomer shift in the same region as \( \text{SbF}_5^- \) and \( \text{SbF}_6^- \) as would be expected for an \( \text{Sb}(V) \) coordinated by six fluorines. The effect of replacing a terminal fluorine in \( [\text{Sb}_3\text{F}_{11}]^- \) by a chlorine to give \( [\text{Sb}_3\text{Cl}_2\text{F}_9^-] \) is to reduce the isomer shift: chlorine being less electronegative than fluorine would withdraw less electron density from the antimony. For both compounds ionic formulations have been implied \( [7, 8] \), but this did not appear to be consistent with their physical properties. A closer reexamination of Preiss's data for \( [\text{SbCl}_4^+] [\text{Sb}_2\text{Cl}_2\text{F}_5^-] \) \( [8] \) reveals a weak, though significant interaction, between cation and anion. A fluorine atom is approximately perpendicular to each face of the \( [\text{SbCl}_4^+] \) tetrahedron giving an overall eight coordination about that antimony. The symmetry about antimony in the cation remains regular and the negligible quadrupole coupling is accounted for. The anion has five fluorines and a chlorine about each antimony and this together with the weaker interaction discussed above would account for the observed quadrupole coupling constant in \( [\text{Sb}_2\text{Cl}_2\text{F}_5^-] \). One might have expected that the antimony site in \( [\text{Sb}_2\text{F}_1] \) would be more symmetrical than in \( [\text{Sb}_2\text{Cl}_2\text{F}_3] \) but this is not the case. The relatively large coupling indicates that there is a similar Sb-F-Sb interaction between cation and anion in \( [\text{SbCl}_4^+] \) \( [\text{Sb}_2\text{F}_1] \). Unfortunately the positional parameters were unavailable for this compound \( [7] \), not allowing us to confirm this suggestion.

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Both \( \text{SbCl}_4^+ \) and \( \text{SbCl}_3\text{F}_3 \) show one site spectra with significant distortions from symmetrical environments. The spectrum of \( \text{SbCl}_4^+ \) is shown in figure 2.

The transmission integral method \( [11, 12] \) was used and the best fit was obtained only when an asymmetry parameter \( > 0 \) was included. \( \text{SbCl}_4^+ \) has been shown to be a tetramer \( [6] \) with cis fluorine bridges completing the octahedral arrangement about each antimony. We have recently obtained X-ray data on \( \text{SbCl}_3\text{F}_2 \) and it too has the tetrameric structure, each antimony having three chlorines, a terminal fluorine and two bridging (cis) fluorines \( [14] \).

In all of the cases where the immediate coordination about the antimony is six, the isomer shift of the nucleus correlates rather well with the relative numbers of coordinated chlorines and fluorines. Antimony pentfluoride with six near fluorine neighbours has the most positive isomer shift, i. e., lowest s electron
density, while SbCl₃F with four chlorines and two fluorines has the lowest shift. Antimony pentachloride and [SbCl₄⁺] have different stereochemistries and would not be expected to conform to this relationship. The isomer shifts of [Sb₂Cl₂F₅⁻] and SbCl₃F₂ fall in the regions expected. We can use this type of correlation to analyze the spectrum of Sb₂Cl₁₁F₄ which shows two partially resolved sites having shifts of 5.3 and 7.7 mm/s. The compound clearly does not contain an [SbCl₄⁺] cation since both shifts are much greater than has been found for this moiety and a structure such as [SbCl₂⁺][Sb₂Cl₄F₇⁻] is ruled out. It may however be possible to prepare this compound and we are presently attempting to do this. [SbF₄⁺]
[Sb₂Cl₁₁] can also be eliminated in the basis of isomer shifts and other chemical evidence. The only reasonable structure which would best fit the evidence is a trimer held together by fluorine bridges with one site (7.7 mm/s) having three terminal chlorines, and a terminal fluorine, and the other site four terminal chlorines. Crystallographic studies on this molecule are currently in progress.

References