NGR SPECTRA OF CERTAIN COMPLEX ANTIMONY(III) FLUORIDES

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UDC 539.166

NGR spectra of complex Sb (III) fluorides of composition MSbF 7 (M = K, Na, Rb, Cs) and Cs 2 SbF 5 were investigated. A qualitative analysis of the obtained results and their comparison with known structural data were carried out.

An investigation of NGR spectra of 125Sb (energy of γ quanta 37.2 keV) in trivalent antimony compounds MSbF 7 (M = K, Na, Rb, Cs) and Cs 2 SbF 5 was carried out. This research is a continuation of our investigations of complex Sb (III) halides [1] for the purpose of obtaining information on the electronic structure of such complex compounds, in the formation of which antimony displays its lower formal valence. For a successful solution of the assigned problem, it is necessary to obtain and analyze NGR spectra for a large number of compounds of known structure. Of the complex trivalent antimony halides the most extensively studied here are the fluorides [2-8]. According to x-ray diffraction data and IR spectra the Sb (III) atom in the M-Sb-F system is characterized by different coordination numbers. It could be expected that these differences will appear in NGR spectra and therefore, the selection of such systems as objects of the investigation is expedient. Interest in such systems has grown lately because they find practical application as new inorganic materials in the electronics industry and optics. Certain complex Sb(III) fluorides have been investigated by the NGR method in [9, 10].

We obtained Mössbauer spectra of 125Sb of the complexes indicated above on an electrodynamic apparatus operating in a constant acceleration regime with a NTA-512 multichannel analyzer. Measurements were carried out at a temperature of ~ 78°K. The source of resonance γ quanta were 125Sb nuclei in a SnO 2 matrix. The investigated samples had a thickness of 4 mg/cm 2 with respect to Sb.

Spectra of the investigated complex fluorides show an asymmetric line, the width of which indicated quadrupole interaction (Fig. 1). The observed maximum values in resonance absorption amount to 8-16%. Analysis of spectra was carried out on an electronic computer by the program of [11], in which the general model of the resonance spectrum is described by eight parameters, including the asymmetry of GEP (η) and anisotropy of Mössbauer effect ε = f(π/2) - f(0) / f(π/2) + f(0). In this program the probability of effect f is presented in the system of spherical functions as

\[ f(0) = f_0 + f_2 P_2(\cos \theta), \]

where θ is the angle between the direction of dispersion of γ quanta and the main axis of the GEP tensor on the nucleus. The obtained values of parameters are presented in Table 1.

It is seen from Table 1 that values of isomeric shifts δ for the compounds MSbF 7 having various cations and for Cs 2 SbF 5 differ from one another. We note that IR spectra of the examined salts are also different [6]. The observed differences are explained by a change in geometric configuration of ligands around Sb (III).

Measured values of δ are presented in Fig. 2 where, for comparison, dependences of isomeric shifts on the differences of electronegativities of the metal halide (ΔX) for simple antimony halides SbX 3 and complex aggregates Cs 2 SbX 9 from [1, 12] are presented. (The value of shift measured by us for SbI 3 δ = 15.8 mm/sec is in good


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Fig. 1. Resonance-absorption spectrum of CsSbF$_7$. $\delta$ (InSb) taken to be equal to zero (isomeric shift of InSb relative to the source $^{111}$InSnO$_2$ equal to 8.55 $\pm$ 0.05 mm/sec).

### TABLE 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$, mm/sec</th>
<th>$\epsilon$, mm/sec</th>
<th>$\eta$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbSb$_2$F$_7$</td>
<td>$-3.20\pm0.1$</td>
<td>$17.8\pm1.2$</td>
<td>$0.0\pm0.4$</td>
<td>$0.0\pm0.2$</td>
</tr>
<tr>
<td>CsSb$_2$F$_7$</td>
<td>$-4.8\pm0.1$</td>
<td>$16.8\pm0.7$</td>
<td>$0.27\pm0.1$</td>
<td>$-0.8\pm0.2$</td>
</tr>
<tr>
<td>Cs$_2$SbF$_5$</td>
<td>$-3.88\pm0.08$</td>
<td>$15.01\pm1.1$</td>
<td>$0.0\pm0.2$</td>
<td>$0.0\pm0.3$</td>
</tr>
</tbody>
</table>

*During analysis of this spectrum parameters $\eta$ and $\epsilon$ were fixed.*

agreement with the value obtained in [12]. It is seen that in the case of trihalides the density of $s$ electrons on the Sb nucleus decreases with increasing differences of electronegativities $[\delta R/R^{(^{111}\text{Sb})} < 0]$, while it increases in the case of complexes CsSbX, on the other hand. This is explained in [1] by the presence of a stereochemically active unshared pair of electrons (UPE) in the valence shell of antimony in the first case and a stereochemically inactive pair in the second. Comparison of data presented in Fig. 2 makes it possible to conclude (independently of x-ray diffraction results) that in complex fluorides of Sb (III) the UPE is stereochemically active.

Next, the point corresponding to the isomeric shift for SbF$_3$ does not lie on the line for trihalides (it is significantly below point A). It is seen from this that antimony trifluoride is not isomeric with SbCl$_3$ and SbBr$_3$. In fact $<\text{ClSbCl}> = <\text{BrSbBr}> \approx 95.5^\circ$, while in the trifluoride one angle is equal to 81.90$^\circ$ and two are equal to 104.3$^\circ$ [13]. In addition, according to the latest papers [3-5] molecules of the trifluoride are joined in a trimer (SbF$_3$)$_3$. The presence of bridge fluorine atoms with a Sb–F bond length of 2.60 Å in the presence of two terminal fluorine atoms with a bond length of 2.03 Å actually decreases the coordination number (CN) of the Sb atom in this compound by one in comparison with the remaining antimony trihalides. For example, if we start from this, the decrease in shift relative to point A and the investigated complexes can be explained first, by a decrease in CN of antimony and second, by the appearance of bridge fluorines.

X-ray diffraction data for CsSb$_2$F$_7$ [8] (Fig. 3) indicate the presence in it of discrete Sb$_4$F$_{17}^-$ anions, which are two trigonal bipyramids (with consideration of UPE), joined by a bridge fluorine. With respect to H$_2$SbF$_5$ complexes [5], they contain discrete Sb$_2$F$_{15}^-$ anions, which can be presented as a distorted octahedron (with consideration of UPE). It is seen from comparison of values $\delta$ for CsSb$_2$F$_7$ and CsSbF$_7$ that the decrease in CN by one and the substitution of one terminal fluorine by a bridge fluorine leads to a decrease in electronic density on the antimony nucleus.