X-RAY DIFFRACTION STUDY OF CRYSTALS OF TRIPHENYLDICHLOROSTIBINE

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The crystal structure of \((C_6H_5)_3SbCl_2\) was determined according to the three-dimensional distribution of electron density with a refinement of the coordinates of individual temperature corrections by the method of least squares. The previously proposed model of the structure was investigated, and it was shown that the compound possesses a molecular structure with molecules in the form of a trigonal bipyramid, in the equatorial plane of which are the phenyl groups, and at the vertices the chlorine atoms.

The structure of \((C_6H_5)_3SbCl_2\) crystals was investigated previously by Stroganov [1], who arrived at the conclusion that "associated cations" \([Sb_2(C_6H_5)_6]^{4+}\), tetrahedrally surrounded by \(Cl^-\) ions, lie at the basis of the structural motif. However, Stroganov himself demonstrated that the crystals of this compound belong to the space group \(P2_1_2_1_2_1\); the antimony atoms form one regular system of points. Since the atoms bonded together only by screw axes in principle cannot create dimer associates, Stroganov's conclusion definitely cannot be correct.

Our repeated x-ray diffraction study indicated that triphenyldichlorostibine possesses a monomer molecular structure. Just as in crystals of \(SbCl_3\), \((CH_3)_2SbCl\) (X = Cl, Br, I) and \((ClCH_2-CH_2)_2SbCl_2\), investigated by other authors [2, 4], the \((C_6H_5)_3SbCl_2\) molecules take the form of trigonal bipyramids with Sb atoms in the center of the bipyramid; in all cases the halogen atoms are situated in the axial vertices of the bipyramid, while the organic ligands (and three out of five chlorine atoms in the case of \(SbCl_3\)) are situated in its equatorial plane.

The preliminary results of the structural investigation, based upon an analysis of the Paterson projections (giving the coordinates of the Sb and Cl atoms) and geometrical analysis, permitting the establishment of the approximate coordinates of the carbon atoms, were published previously [5]. This work presents the details of the structural investigation and the results of a refinement of the coordinates of all the atoms, including the carbon atoms, according to the complete three-dimensional set of diffraction rings.

SYNTHESIS AND CRYSTALLOGRAPHIC CHARACTERISTICS

The compound \((C_6H_5)_3SbCl_2\) was produced by the method of double diazonium salts, discovered by Nesmeyanov [6], for the example of organomercury compounds, and developed for organoantimony compounds by Nesmeyanov and Kocheshkov [7]. The double salt of phenyl diazium chloride and antimony trichloride (May's salt) is decomposed by zinc dust in an organic solvent; in this case a mixture of several compounds is obtained: \(C_6H_5SbCl_2\) (basic product), \((C_6H_5)_2SbCl\), \((C_6H_5)_3Sb\) and \((C_6H_5)_2SbCl_2\) (side products). Variation of the conditions of the reaction and treatment of the reaction mixture [8] leads to a change in the amounts of the organoantimony compounds formed, as well as to a decrease in their number. In the case of a vigorous course of the reaction, which is achieved by shaking of the reaction mixture, up to 18% of the compound \((C_6H_5)_3SbCl_2\) with m.p. 142-143\(^\circ\) can be obtained. Single crystals were produced by slow evaporation of a solution of \((C_6H_5)_3SbCl_2\) in chloroform.

Transparent colorless crystals of \((C_6H_5)_3SbCl_2\) take the form of plates and belong to the rhombohedral symmetry type. Simple forms were developed: prism \([110]\), tetrahedron \([111]\) and \([\{111\}\) (Fig. 1). According to goniometric data, \(a:b:c=1.19:1.11:1.133\). The parameters of the cell, refined in the KFOR camera with NaCl standard: \(a = 13.17 \pm 0.03\); \(b = 11.08 \pm 0.03\); \(c = 12.39 \pm 0.03\) \(\AA\), \(N = 4\), \(\text{d}_{\text{pycn}} = 1.55\), \(\text{d}_{\text{x-ray}} = 1.56 \text{g/cm}^3\). The space group \(P2_1_2_1_2_1\) is unambiguously determined according to the extinctions. The presence of a piezo effect (data of V. A. Koptski, Moscow State University) agrees with the noncentrosymmetric character of the space group found.
CHARACTERISTICS OF THE EXPERIMENTAL DATA

An x-ray diffraction study of triphenyldichlorostibine was conducted according to developments of the layer lines attained in the KFOR camera in Mo-Kα radiation. The zero layer lines were taken in rotation around three coordinate axes: [001], [100], and [010], and the first to eighth layer lines in rotation around the axis [001]. The x-ray diffraction patterns contain 106 rings of the type hko, 126-0k/, 133-0k/ and 850-hkl. The bulk of the experimental data were obtained with fragments of crystals, close to columnar in shape. These data were used to calculate the Paterson projections on three coordinate planes, as well as the three-dimensional distribution of the electron density. The intensities of the reflections of the zero layer lines were subsequently refined according to photographs obtained from spherical samples 0.15-0.17 mm in diameter, which were oriented according to the Laue powder patterns first in the RKOP camera, then in the KFOR camera [9]. Three to four photographs with multiple exposures were obtained along each direction. The intensities were estimated visually by marks of blackening containing 27 spots.

In the calculation of the structural factors, we considered the kinematic and polarization factors; the absorption factor was not taken into consideration. The ratio \( \frac{|F_{\text{max}}|^2}{|F_{\text{min}}|^2} \) was equal to 436:1 for diffraction rings of the type hko; 238:1 for h0k; and 316:1 for 0hk; \((\sin \theta/\lambda)_{\text{max}} = 0.75\).

DETERMINATION OF THE COORDINATES OF THE Sb AND Cl ATOMS

Since in the P212121 group there are only common (quadruple) positions, all the atoms of the formula unit of \((C_6H_5)_3SbCl_2\) are symmetrically independent, and the structure possesses 63 coordinate parameters, not considering the parameters of the hydrogen atoms.

The positions of the antimony atoms were determined according to the Paterson projections on the three-coordinate planes. The coordinates of the Cl atoms were obtained from the Paterson projections by the method of superposition, using the operation \(\min[F(u + u_0)]\) as the function of isolation. At this stage of the investigation, the following values were obtained for the coordinates of the heavy atoms Sb and Cl:

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
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<tbody>
<tr>
<td>Sb</td>
<td>0.229</td>
<td>0.372</td>
<td>0.729</td>
</tr>
<tr>
<td>ClI</td>
<td>0.225</td>
<td>0.162</td>
<td>0.811</td>
</tr>
<tr>
<td>ClI1</td>
<td>0.220</td>
<td>0.580</td>
<td>0.644</td>
</tr>
</tbody>
</table>

The atoms ClI, Sb and ClI1, within the limits of error, are situated on the same straight line, and the distances ClI-Sb and Sb-ClI1 are approximately the same.

DETERMINATION OF THE COORDINATES OF THE CARBON ATOMS

Calculation of the projections xy and xz of the electron density in a first approximation (with signs of the structural amplitudes according to the coordinates Sb, ClI, and ClI1) permitted a refinement of the coordinates of the antimony and chlorine atoms but did not give any information on the arrangement of the light atoms.

However, on the basis of the arrangement of the Sb and Cl atoms and the literature data on the concentration of the molecules \((CH_3)_3SbX_2\) and \((CICH = CH)_3SbCl_2\), it might have been assumed that the molecules possess a trigonal bipyramid structure. The problem consequently consisted of finding only four parameters: the angle of rotation of the bipyramid \(\psi\) around its principal axis—the line of the ClI-Sb-ClI1 bonds and the angles of rotation of the three phenyl groups \(\phi_1, \phi_2,\) and \(\phi_3\) around the lines of their bonds with the antimony atom. Geometrical analysis, conducted on the Kitaigorodskii structure finder [10], gave a single solution for the problem.

The determination of the tentative values of the coordinates of all the carbon atoms permitted a refinement of the system of signs of the structural amplitudes. Nonetheless, originally not one of the 18 maxima of the carbon atoms appeared upon the projections of the electron density. However, after repeated x-ray diffraction patterns, taken from spherical samples, were obtained, with a careful evaluation of the intensities (using the method of multiple exposures), the quality of the projections of the electron density were sharply improved.

The projections are presented in Figs. 2 and 3. The phenyl groups appear quite distinctly and confirm the data of the geometrical analysis. Of the 18 carbon atoms in the projection xz, only one falls in a region with a low value of the density.