Mixed halides of mercury were synthesized more than a hundred years ago [1-3], and now, thanks to systematic investigations, their nature has been entirely elucidated. Thus, it has been shown by methods of crystal chemistry and physicochemical analysis that mixed crystals, which undergo phase transformations when the relative concentrations of the halogens are changed, are formed in the systems \( \text{HgX}_2 - \text{HgY}_2 \) [4-6]. In view of this, it was of interest to study the properties of mixed halides of the \( \text{HgXY} \) type, produced by various methods: 1) by the action of dry halogen \( X_2 \) on the crystalline salt \( \text{Hg}_2\text{Y}_2 \); 2) by the action of the halogen \( X_2 \) on an alcohol suspension of \( \text{Hg}_2\text{Y}_2 \); 3) by pouring together alcohol solutions of equimolar amounts of \( \text{HgX}_2 \) and \( \text{HgY}_2 \). It is quite probable that the difference in the methods of production may lead to a difference in the crystallographic forms of the mixed crystals of the same composition, especially when such oxidation reactions as

\[
\text{Hg}_2\text{X}_2 + \text{Y}_2 \rightarrow 2\text{HgXY} \quad \text{and} \quad \text{Hg}_2\text{Y}_2 + \text{X}_2 \rightarrow 2\text{HgYX}
\]

are carried out. Hence, the purpose of this work was the synthesis and refractometric, x-ray diffraction, and thermographic study of mixed halides of divalent mercury.

**EXPERIMENTAL**

To economize on space, in our further exposition the following terminology will be used to denote the order of addition of the halogens: mercuric chlorobromide \( \text{HgBrCl} \), denotes the product obtained by adding an atom of chlorine to \( \text{HgBr} \); mercuric iodobromide \( \text{HgBrI} \), corresponds to the addition of iodine to \( \text{HgBr} \), etc. The numbers in parentheses will denote the methods of production: \( \text{HgClII} \) (I) denotes the product obtained by fusing crystalline mercurous chloride with iodine; \( \text{HgBrCl} \) (II) was produced by chlorination of an alcohol suspension of mercurous bromide; \( \text{HgBrI} \) (III) was prepared by pouring alcohol solutions of \( \text{HgBr}_2 \) and \( \text{HgI}_2 \) together. Mercuric bromochlorides, synthesized by the three methods (the oxidation reactions proceed very rapidly), possess practically the same compositions, as is evident from the results of analysis for the total halogens. Found for \( \text{HgClBr} \): (1) 36.25%; (2) 36.51%; (3) 36.27%. Calculated for \( \text{HgClBr} \): 36.51%. In all cases the analysis was performed by gravimetric method; the sample (about 0.2 g) was boiled for 2 h in a concentrated solution of alkali, then the filtrate was neutralized, and a solution of \( \text{AgNO}_3 \) was added to it. All the bromochlorides are not entirely soluble in alcohol and are decomposed by alkalis. \( \text{HgClBr} \) (I) also does not dissolve entirely in water and acids, while samples of (II) and (III) dissolve slowly in water, \( \text{HNO}_3 \), and \( \text{H}_2\text{SO}_4 \), but rapidly in HCl.

Figure 1 presents thermograms of the bromochlorides, together with \( \text{HgCl}_2 \) and \( \text{HgBr}_2 \), from which the small difference in the properties of \( \text{HgClBr} \) produced by different methods is evident. The measurement of the temperatures here and subsequently was performed with standard Pt-Rh thermocouples, with an accuracy of \( \pm 1.5 \)°; the heating curves were recorded on the FPK-59 pyrometer, rate of heating 10.5-11.5 deg/min, standard substance \( \text{Al}_2\text{O}_3 \). Figure 2 presents line diagrams depicting the x-ray diffraction patterns of the bromochlorides, from which it can also be concluded that there is a certain difference in the \( \text{HgClBr} \) samples produced by different methods. Photography was conducted in copper radiation with a Ni filter in an RKD-57 chamber. Finally, Table 1 presents the results of a crystallo-optical investigation of mercuric bromochlorides, as well as their densities, measured by a pycnometric method.
Fig. 1. Thermograms of mercuric chloride-bromides: 1) HgCl₂; 2) HgClBr (I); 3) HgClBr (II); 4) HgClBr (III); 5) HgBrCl (II); 6) HgBr₂.

Fig. 2. X-ray diffraction patterns of halides of the series HgCl₂–HgBr₂: 1) HgCl₂; 2) HgClBr (I); 3) HgClBr (II); 4) HgClBr (III); 5) HgBrCl (II); 6) HgBr₂.

TABLE 1. Refractometric Constants of HgClBr

<table>
<thead>
<tr>
<th>Sample</th>
<th>d₄²₅</th>
<th>nₐ</th>
<th>nₘ</th>
<th>nₚ</th>
<th>nD</th>
<th>MR</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgClBr (I)</td>
<td>5,90</td>
<td>≈2.06</td>
<td>1,598</td>
<td>1,899</td>
<td>≈1,984</td>
<td>≈26.4</td>
</tr>
<tr>
<td>HgClBr (II)</td>
<td>5,99</td>
<td>≈2.06</td>
<td>1,939</td>
<td>1,877</td>
<td>≈1,957</td>
<td>≈25.6</td>
</tr>
<tr>
<td>HgClBr (III)</td>
<td>5,75</td>
<td>2.03</td>
<td>1,975</td>
<td>1,819</td>
<td>1,939</td>
<td>25.3</td>
</tr>
</tbody>
</table>

From Table 1 we can see the distinct differences in the indices of refraction of samples of different origin and the closeness of their molar refractions, which indicates the same nature of these substances.

Mercuric iodochloride was produced according to the first method by heating Hg₂Cl₂ with exactly twice the amount of the halogen for 6 h at 130°. The excess iodine was washed out with a stream of benzene. In the iodination with an alcohol solution, exactly twice the amount of iodine was also used. In the first case, the solution of Hg₂Cl₂ proceeded slowly, in the second, considerably more rapidly. In the evaporation of the alcohol solution in a stream of air at 50–60°, in both cases a red crystalline powder remained, containing practically no free iodine. Evidently the excess amount of halogen was volatilized together with the alcohol vapors. Solutions of Hg₂Cl₂ and HgI₂ in absolute alcohol were used to produce HgClI (III). The sum of the halogens for the composition HgClI comprises 43.93%. Found for HgClI: (I) – 45.50; (II) – 44.88; (III) – 45.94%. Mercuric iodochlorides are red powders, insoluble in water, organic liquids, and cold acids (HCl, HNO₃, and H₂SO₄), but dissolve in these acids upon heating. The indices of refraction of HgClI (I), (II), and (III) are above 2.4; the densities are correspondingly equal to 5.89, 5.78, and 5.85. The thermograms cited in Fig. 3 indicate a small difference, just like the x-ray diffraction patterns, the graphical depiction of which is given in Fig. 4.

Mercuric iodobromides were prepared analogously to the iodochlorides. All three samples represent greenish-yellow powders, insoluble in water, organic liquids, and cold acids (HCl, HNO₃, and H₂SO₄). Upon boiling in the first two acids, complete solution occurs, while in concentrated H₂SO₄, the iodobromides first dissolve upon heating, but then a white precipitate is deposited. For the formula HgBrI, the sum of the halogens should comprise 50.76%, while analysis gives for HgBrI: (I) – 49.39; (II) – 49.54; (III) – 50.67%. The thermograms of mercuric iodobromides (Fig. 5) are practically identical, while their x-ray diffraction patterns (Fig. 6) show an appreciable difference,