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An Experimental Study of Formation of the Mercury Mixed Halides HgClBr and HgBrI and of Their Purity

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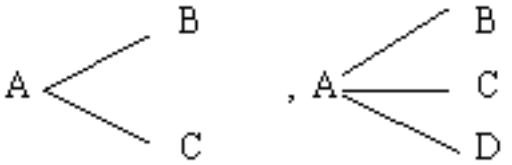
ABSTRACT

Claims to have produced the mixed halides of mercury are very old. However, their stability or even their very existence was seriously questioned by Ammlung and Brill several decades back, on the basis of their study, in several solvents, of what was thought to be HgBrI. The mixed halide HgCII was already known to be unstable. On the basis of these facts, which were also lent some theoretical support, it was strongly conjectured that the mixed halides of mercury and similar elements, were expected to be unstable. However, the matter does not seem to have received the attention it deserved. It was in this light that this study was taken up. What has been thought to be HgClBr has been produced by several methods and HgBrI by one or rather two methods. The product has been subjected to X-ray diffraction, FTIR and Raman studies. Studies confined to the solid product are being reported here and only those results are being presented for which all the three techniques could be employed. These studies show that a new product is indeed formed in most of these cases, but the product is not pure in any of these cases, although the impurity seems to be quite small in most of these cases. This calls for having a thorough look at not only the mixed halides of the elements, but of all compounds claimed to be like:



etc.

Key words: Mixed halides, impure product, d-values, FTIR Studies.

INTRODUCTION

Mercury has been known for a long time and its compounds studied[1]. Claims to have produced mixed halides of mercury go fairly long back into time[2]. However, Ammlung and Brill and others have thoroughly studied the problem and these authors have seriously challenged existence of the mixed halides[3, 4]. Ammlung and Brill carried out a study of the Raman lines of what was claimed to be HgBrI, dissolved in some solvents. They found strong Raman lines of the constituent di-halides of mercury[3]. The mixed halide HgClI had already been found to be highly unstable. Some theoretical support to this idea was also indicated.

However, rather surprisingly, almost no notice of Ammlung and Brill's work seems to have been taken for quite a long time. Workers continued to claim formation of the di-halides of not only mercury but also of cadmium and zinc[5,6]. Claims have been made of determination of structures of mixed mercury halide crystals[7]. Nobody seems to have thoroughly investigated the extent of the correctness of these claims.

We seem to be the first workers to have thoroughly investigated what seems to be HgClBr and to some extent HgBrI also. The main reason was that Ammlung and Brill had confined their study only to what was thought to be HgBrI dissolved in some solvents. We have extended our study to not only what would be regarded as HgBrI but much more extensively to what would be regarded as HgClBr. Besides considering many more solvents, we have additionally studied the product in the solid state. This work is concerned only with the product mixed halide in the solid state.

We briefly mention the different ways in which what is regarded as HgClBr has been prepared, using the methods suggested in the literature as well as some of our own. Earlier some X-ray studies of the products formed by these methods have been taken up by some authors[8].

We have produced what would be regarded as HgClBr by several methods and have also produced what would be regarded as HgBrI by two methods. All these methods are given below.

Preparation of HgClBr

Method I

By heating an equmolar mixture of $HgCl_2$ and $HgBr_2$ in an oven at 80°C, for 48 hours (The same reaction has also been carried out at 100°C and 150°C for 10 hours in each case).

$$HgCl_2 + HgBr_2 \rightarrow HgClBr$$

Method II

In the method of preparation, a saturated solution of $HgCl_2$ and $HgBr_2$ in water mixed in 1:1 ratio, was kept in a desiccator over $CaCl_2$ until solid crystals separate out

$$HgCl_2 + HgBr_2 \rightarrow 2HgClBr$$

HgClBr produced by this method is in nanoform[9]. Several methods are available for grain size measurements[e.g.10]. However, we have used the Debye-Scherer formula[11].

Method III

In the method due to R.P. Rastogi, bromine gas is passed over solid mercurous chloride until a constant weight is obtained[7]

$$Hg_2Cl_2 + Br_2 \rightarrow 2HgClBr$$

Preparation of HgBrI

Method I

HgBrI was prepared by mixing equimolar solutions of $HgBr_2$ and HgI_2 in acetone. Crystals of HgBrI separated after evaporation

$$HgBr_2 + HgI_2 \rightarrow 2HgBrI$$

Method II

An equimolar mixture of $HgBr_2$ and HgI_2 is taken and then to grind the two halides together at room temperature. This is called Type-II mixture.

Type I and Type II mixture and use of the X-ray d values for identification of a new product

X-ray d-values are extensively used for identifying the compounds present in a mixture. The standard practice is to locate the three most prominent peaks of the compound for its identification. The most important matter is to decide how much deviation in the d-values is permissible.

This is what we find out.

Extension of this approach for concluding if a new product has been formed in a reaction is direct and straightforward. This is discussed here.

One needs the diffractogram of the constituent reactants and additionally the diffractogram of an equimolar mixture of the reactants, when they are separately ground and then added to each other, is very helpful. This type of equimolar mixture may be called the Type-I mixture. We discuss a simple case as an illustration.

We have taken the diffractograms of $HgCl_2$, $HgBr_2$ and of their Type-I mixture. These are given in Figs. 1, 2 and 3 respectively. We prepare the equimolar mixture in another way also. We take suitable equimolar amounts, mix these and grind these in a mortar. We call it the Type-II mixture. The diffractogram is given in Fig. 4. The d-values for the above cases are given in Tables 1-4, respectively.

One would expect no chemical or even physical change to have occurred in the Type I mixture. Therefore, it may be taken to give the shifts in the d-values that would be expected to occur in a mixture of these compounds. Greater shifts from those noted here would be regarded as belonging to a new compound. A totally new peak would be an unmistakable signal for the formation of a new compound. Occurrence of peaks of the reactants within the permissible range, as determined from the Type I mixture, would be regarded as a signal that these represent presence of some unused reactant. However, in some cases, these might well belong to a new compound.

With this background in mind we study the data of the mercury halides and their mixtures mentioned above.

By comparing the three most prominent peaks of $HgCl_2$ and the single most prominent peak of $HgBr_2$ (all the other peaks of $HgBr_2$ being very insignificant), with the corresponding peaks in the Type I mixture we can find out the maximum permissible deviation in the d-values, of a prominent peak, when the compound be present in a mixture.

By the above comparison, we may ascribe the maximum deviation to the d-values of 2.6263 (a_1) in the Type I mixture, if we identify it with the d-value of 2.7022(α_1) in $HgCl_2$ with an intensity of 57.7%. This would be about 0.08°A. However, if we identify the peak at d=2.8121 (α_1), in the Type-I mixture, with the d value of 2.7022 (α_1) in $HgCl_2$, the permissible deviation would be about 0.1°A. To be on the safe side, we take the latter to be the permissible deviation for $HgCl_2$ in a mixture. Any difference in the d-value within 0.1°A from those for the $HgCl_2$ peaks would be taken to signal presence of $HgCl_2$ but d-values outside the maximum upper limit would generally mean absence of $HgCl_2$ and presence of some other compound. We see that for all the other prominent peaks of $HgCl_2$ and $HgBr_2$, the expected deviation to be much less than 0.1°A. However, the deviation of the d-values may be larger if the number of compounds in the mixture is large. We may finally add that d-values should always be seen in conjunction with the relative intensity.

In the above light, we examine our products. The presence of the most prominent peak at δ = 3.1239, in the Type II mixture, is a clear indication of the formation of a new product. However, presence of a fairly strong peak at d =6.1972 may be taken as a clear indication that $HgBr_2$ is also present in the Type II mixture along with the new product. By comparing its peak intensity counts of 213 with the corresponding counts of 666 in the Type I mixture, we may conclude that the amount of the $HgBr_2$ along with the new product, is about 16%.

Summary of the analysis of the X-ray diffractograms

Occurrence of a new prominent peak which is not found in the diffractogram of either of the reactants, may be taken as a strong evidence for the formation of a new product.

If a prominent peak considered as belonging to a reactant is found to have suffered a displacement which is more than what may be regard as permissible. (say, a maximum value of 0.1° A in the d-values, for our system), that may also be taken as belonging to a new product.

Relative intensity consideration is often helpful in assigning a peak to a reactant.

Density Considerations

If the density of a compound AB_2 is denoted by d_{AB_2} and its molecular weight by M_{AB_2}, it can be easily seen that the density *D* of a well-packed equimolar mixture of the compounds AB_2 and AC_2 is given by

$$D = \frac{\left(M_{AB_2} + M_{AC_2}\right) d_{AB_2} d_{AC_2}}{\left(M_{AB_2} d_{AC_2} + M_{AC_2} d_{AB_2}\right)}$$

Taking the densities of $HgCl_2$ and $HgBr_2$ obtained from the standard literature as also their molecular weights[12], we get the density *D* of their equi-molar mixture. The densities of $HgCl_2$ and $HgBr_2$ are given in Table-5, along with the density of HgClBr, as prepared by Method-I. The density regarding HgClBr as an equimolar mixture of $HgCl_2$ and $HgBr_2$ is given inside the bracket. The value of the density for what is called HgClBr is that measured by one of the authors (R.Ahmad). The melting points are taken from ref.12 and are given in Table 5.

The results encourage us to believe that HgClBr (Method-I) is largely a new product. A small fraction of the constituent reactants cannot be ruled out.

Results of the examination of the product and the conclusions

We may examine the products of the reactions using the criteria arrived at above. In this study, we have included only those products for which the X-ray d-values, the FTIR absorption wave numbers as well as the wave numbers of the Raman lines are available. The results are given below (the wave numbers are in cm^{-1}).

1.	$HgCl_2$ + $HgBr_2$ (Type II mixture)	The X-ray study indicates presence of a relatively small fraction of the reactants along with a new product. T h e FTIR and the Raman do not show any wave numbers of the reactants.
2.	HgClBr (Ist Method) : Heating the equimolar mixture, at 80°C, for 48 hours.	The X-ray study indicates a fairly pure product. The FTIR no wave-number of the reactants. The Raman shows the $HgCl_2$ wave numbers 312.302 and 381.301.
3.	HgClBr (IInd Method)	The X-ray study indicates a small fraction of the reactants along with a new product. The FTIR shows the $HgBr_2$ wave number 835.0430. The Raman does not show any lines of the reactants.
4.	HgClBr (IIIrd Method)	The X-ray study indicates presence of the reactants, possibly along with a new product. The FTIR shows the $HgBr_2$ wave number 835.0436 and 1916.936. The Raman does not show any lines of the reactants.
5.	$HgBr_2$ + HgI_2 (Type II mixture)	A new product has been formed. The X-ray study does not indicate presence of the reactants. The FTIR shows the HgI_2 wave number 1610.303. The Raman does not show any lines of the reactants.
6.	HgBrI	The new product could be reasonably pure. The FTIR shows the HgI_2 wave number 1384.668. The Raman does not show any lines of the reactants.

Table 1: $HgCl_2$

Angle [°2θ]	d-values α1[°A]	d-value α2[°A]	Peak Intensity [Counts]	Rel. int [%]
20.335	4.3635	4.3744	246	100
21.620	4.1070	4.1172	83	33.6
24.860	3.5786	3.5875	21	8.6
25.375	3.5071	3.5158	20	8.2
26.350	3.3795	3.3879	90	36.6
28.035	3.1801	3.1880	23	9.3
29.085	3.0676	3.0753	40	16.1
29.415	3.0340	3.0415	86	35.1
29.875	2.9883	2.9957	174	70.7
33.125	2.7022	2.7089	130	57.7
37.230	2.4131	2.4191	69	27.9
41.390	2.1797	2.1851	61	24.7
42.415	2.1293	2.1346	69	27.9
43.860	2.0625	2.0676	41	16.6
45.225	2.0033	2.0083	100	40.6
46.835	1.9382	1.9430	42	17.1
47.830	1.9001	1.9049	49	19.9
50.945	1.7910	1.7955	55	22.2
51.570	1.7708	1.7752	16	6.5
52.185	1.7513	1.7557	14	5.9
55.085	1.6658	1.6699	26	10.6
56.900	1.6169	1.6209	23	9.3
57.885	1.5917	1.5957	12	4.7
58.275	1.5820	1.5859	20	8.2
60.195	1.5360	1.5399	20	8.2
62.980	1.4746	1.4783	21	8.6
64.025	1.4531	1.4567	18	7.2
66.490	1.4051	1.4085	19	7.9

Table 2: $HgBr_2$

Angle [°2θ]	d-values α1[°A]	d-value α2[°A]	Peak Intensity [Counts]	Rel. int [%]
214.345	6.1693	6.1846	1076	100
24.275	3.6635	3.6726	88	8.2
27.370	3.2558	3.2639	74	6.9
31.950	2.7988	2.8058	83	7.7
38.785	2.3199	2.3256	62	5.8
43.885	2.0614	2.0665	137	12.7
44.660	2.0274	2.0324	64	5.9
59.685	1.5479	1.5518	81	7.5
59.875	1.5435	1.5473	96	8.9

With the possible exception of the third method for producing HgClBr, in all the other cases, including those for producing HgBrI, a new product which may be regarded as a mixed halide of mercury, is formed, but in all these cases, a small quantity of the constituent di-halides is present along side the mixed halide of mercury. By Method –II of producing HgClBr nano form of HgClBr has been produced. It is clearly seen from all the three studies that the product in each cases is somewhat different. It is intriguing that probably small quantity of one of the reactants remain. This might mean that in a small number of cases a more complicated additive compound is formed. Probably this is arising not due to the instability of the compound formed but due to the formation of a complicated additive compound.

Since all the three kinds of data are not available for the two other slight modifications of

Table 3: Room temperature equimolar mixture when $HgCl_2$ and $HgBr_2$ are separately pressed and mixed without applying any significant pressure (Type-I)

Angle [°2θ]	d-values α1[°A]	d-value α2[°A]	Peak Intensity [Counts]	Rel. int [%]
14.285	6.1951	6.2105	666	100
19.675	4.5084	4.5196	37	5.6
20.425	4.3445	4.3553	121	18.2
23.270	3.8194	3.8289	36	5.4
24.355	3.6516	3.6607	193	29.0
27.365	3.2564	3.2645	240	36.1
29.950	2.9810	2.9884	86	13.0
31.795	2.8121	2.8191	149	22.4
32.200	2.7776	2.7845	37	5.6
34.110	2.6263	2.6329	100	15.0
37.235	2.4128	2.4188	50	7.6
38.850	2.3161	2.3219	58	8.7
43.330	2.0865	2.0917	79	11.9
44.490	2.0347	2.0398	38	5.8
45.165	2.0059	2.0109	50	7.6
46.935	1.9343	1.9391	67	10.1
49.920	1.8254	1.8299	38	5.8
59.335	1.5562	1.5601	55	8.2
65.645	1.4211	1.4246	38	5.8
66.025	1.4138	1.4173	55	8.2

Method-I for producing HgClBr, these are not being discussed here. The same applies to the product obtained by the application of high pressure to a pellet of an equimolar mixture of $HgCl_2$ and $HgBr_2$ or $HgBr_2$ and HgI_2.

We like to carry out the required analysis that remains in these cases and then to hopefully report these results. However, it seems likely that the mixed halides would have some fraction of the constituent di-halides.

Table 4: Room temperature equimolar mixture of $HgCl_2$ and $HgBr_2$(pressed in mortar) Type-II

Angle [°2θ]	d-values α1[°A]	d-value α2[°A]	Peak Intensity [Counts]	Rel. int [%]
14.280	6.1972	6.2126	213	47.9
19.590	4.5278	4.5390	388	87.2
20.360	4.3582	4.3691	100	22.5
21.215	4.1845	4.1949	53	12.0
25.600	3.4768	3.4854	59	13.3
28.230	3.1586	3.1664	119	26.7
28.550	3.1239	3.1317	445	100
29.380	3.0375	3.0451	40	8.9
29.910	2.9849	2.9923	25	5.6
32.155	2.7814	2.7883	159	35.7
35.865	2.5018	2.5080	61	13.7
39.945	2.2551	2.2607	32	7.3
40.970	2.2010	2.2065	79	17.8
42.590	2.1210	2.1263	64	14.4
43.845	2.0631	2.0683	86	19.4
45.245	2.0025	2.0075	37	8.4
45.695	1.9838	1.9888	77	17.4
49.810	1.8291	1.8337	38	8.6

Table 5:

Compound	Experimental Density (gm/ c.c.)	Melting point (°C)
$HgCl_2$	5.44	276
$HgBr_2$	6.11	236
HgClBr	5.3 (5.8)*	205

* The density on the assumption that this is an equimolar mixture of $HgCl_2$ and $HgBr_2$.

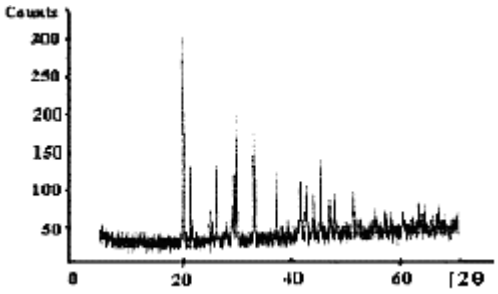


Fig. 1: $HgCl_2$

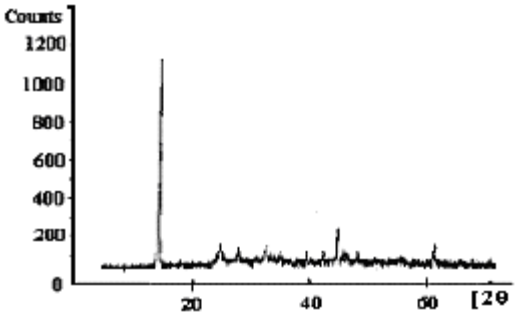


Fig. 2: $HgBr_2$

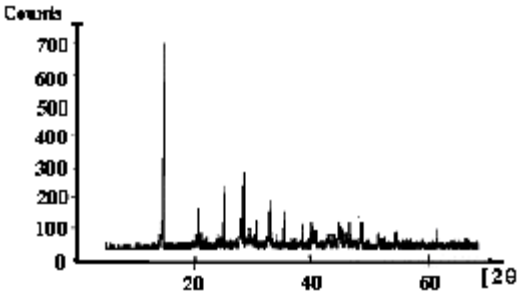


Fig. 3: Equimolar mixture of $HgCl_2$ and $HgBr_2$ at room temperature (Type I)

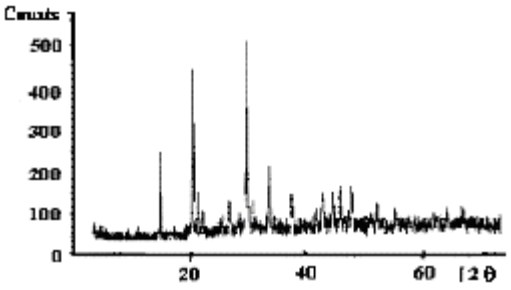
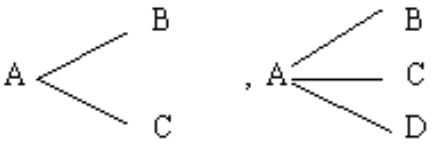


Fig. 4: Equimolar mixture of $HgCl_2$ and $HgBr_2$ at room temperature (Type II)

In this light one may have a critical experimental study of the mixed halides of other elements. In fact, one may examine any compounds of the form



etc., in this light one should also have a look at the claims of having produced the single crystals of the mixed halides. Other methods for producing the mixed halides may still be tried out. Use of nano-reactants may make a difference.

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