X-Ray Study of Hg_2Cl_2–Br_2 and $HgCl_2$–$HgBr_2$ Reactions in Solid State

SAFIA MEHDI

Regional Research Laboratory, Hyderabad, Andhra Pradesh, India

AND S. MUMTAZ ANSARI*

Department of Chemistry, Aligarh Muslim University, Aligarh, U.P., India

The reactions (I) $Hg_2Cl_2(s)$ + $Br_2(g)$ and (II) $HgCl_2(s)$ + $HgBr_2(s)$ have been investigated by an X-ray method. Both the reactions yield two forms of the mixed halide HgClBr, designated as α-HgClBr and β-HgClBr. The cell parameters of the two are as follows:

α-*HgClBr:* a = 6.196 Å, b = 13.12 Å, c = 4.37 Å, z = 4, ρ = 5.91 g/cm³. The powder pattern and cell parameters are similar to that of $HgCl_2$. Therefore it is probable that the chlorine atoms, in the linear halogen–Hg–halogen molecules of $HgCl_2$ structure have been replaced by bromines, and since the radius of the bromine atom is larger than that of chlorine, the lattice is larger in this case.

β-*HgClBr:* a = 6.78 Å, b = 13.175 Å, c = 4.17 Å, z = 4, ρ = 5.40. These parameters are the same as those reported in the literature for β-Hg(ClBr)₂, and its X-ray powder pattern is similar to $HgCl_2$. Therefore this phase also has linear halogen–Hg–halogen molecules but the distribution of Cl and Br atoms is perhaps random.

Heating the products (I) and (II) up to the melting point increases the amount of α phase and decreases the β phase, whereas crystallization increases the β phase. DTA study has supported the X-ray findings.

In solid state chemistry the crystalline matrix provides extraordinary spatial control on the initiation and progress of reactions. This control manifests itself as subtle geometrical and structural effects on molecular reactivity. A knowledge of the geometry of the crystal lattice is thus very useful in understanding the mechanism of solid state reactivity. One of the simplest and probably the most direct method of identifying the various crystalline states formed in the reactions is X-ray diffraction analysis. These facts prompted us to undertake

X-ray investigation of the following solid-state reactions:

I. Mercurous chloride (solid) treated with bromine (gas) at room temperature.

II. Mercuric chloride (solid) treated with mercuric bromide (solid) at 90°C.

Experimental

For reaction I, a known amount of solid mercurous chloride, Hg_2Cl_2 (BDH, AR grade) was made to react with bromine gas (BDH, AR grade liquid bromine was used to get the bromine vapors). The weight of Hg_2Cl_2 was measured at regular intervals.

* Present address: Institut Physikalische Chemie and Elektrochemie, Universitat Hannover, 3000 Hannover 1, West Germany.

When the product attained a constant weight it was separated and kept in a thermostat for several hours to allow the unreacted bromine to escape.

For reaction II, solid mercuric chloride (BDH, AR) powdered to 200 mesh was mixed with solid mercuric bromide (E. Merck grade) in 1 : 1 molar proportions and kept in an oven at 90°C in a closed porcelain dish. The product was analyzed after every 3 hr until there was no sign of any of the starting materials. The mixture was kept at this rather low temperature and in a closed container in order to avoid any possibility of deviation from 1 : 1 molar proportion due to the higher degree of sublimating property of the reactants.

Procedural details of the above reactions will be published elsewhere. X-Ray powder diffraction patterns of the reaction products were taken on a Philips X-ray diffractometer fitted with a copper target. A nickel filter was used to get $CuK\alpha$ radiation. The positions of the reflections were obtained using calcite as standard. Intensities were estimated from peak heights, the height of the strongest being taken as 100 units in each case.

The single-crystal method was used to determine the unit cell parameters of the compounds. Crystals could be grown by heating the reaction products close to their melting points and then suddenly cooling. These were needle shaped and of a size sufficient for X-ray analysis. Cell parameters were determined with the help of both Nonius Weissenberg and precession cameras.

Melting points were determined by KOFLAR micro hot stage.

In order to supplement X-ray results DTA curves were also taken with the help of an automatic DTA apparatus, Leeds and Northrup model. The heating rate was 10.0°C/min.

Table I gives indexed X-ray powder data of (i) reaction product I at room tempera-ture, (ii) after heating it to 120°C, (iii) to 220°C, (iv) the same after recrystallization in alcohol, and (v) the calculated d values along with the corresponding indices.

Table II gives indexed X-ray powder data of reaction product II (i) at room temperature, (ii) after heating to 120°C, (iii) after heating to 220°C, (iv) after heating to 255°C, and (v) the calculated d values along with the corresponding indices.

Figure 1 gives the DTA curves of the two reaction products.

Results and Discussion

The X-ray powder pattern of reaction product I shows the presence of two compounds. These have been designated as the α and β phase of the double compound HgClBr. The reaction seems to take place as follows:

Hg_2Cl_2 (solid) + Br_2 (gas) →
$$\alpha\text{-HgClBr} + \beta\text{-HgClBr (trace)}.$$
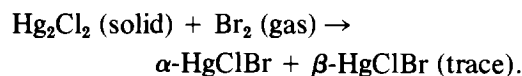
The pattern of the α phase is very strong whereas that of the β phase is very weak. The former is very similar to the pattern of $HgCl_2$ (4), the d values being higher than that of $HgCl_2$. On heating the product to 120°C the α phase pattern becomes stronger and that of the β phase weaker. At 225°C only the α phase pattern remains. On further heating to 240°C the product melts and on sudden cooling it crystallizes.

Using these crystals to get Weissenberg and precession photographs the following cell parameters were obtained:

$a = 6.196$ Å, $b = 13.120$ Å,
$$c = 4.39 \text{ Å, } Z = 4, \rho_{calc} = 5.91.$$

The symmetry is orthorhombic. The space group is *Pnmb*. X-ray data thus suggest that the structure of α phase is very similar to that of $HgCl_2$. Probably alternate chlorine atoms, in the linear halogen–Hg–

TABLE I

X-RAY POWDER DATA FOR REACTION PRODUCT I

| Reaction product I | | | | | | | | | |
| At room temperature | | At 120°C | | At 220°C | | Recrystallized in alcohol[a] | | | |
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d_{calc}(Å)	hkl
—		—		—		6.02	56	6.028	110
4.72	11	4.67	4	—		4.72	83	4.724	120
4.50	95	4.48	100	4.48	100	4.52[b]	7		
4.16	66	4.11	42	4.11	60	4.17	5	4.170	001
—		—		—		3.97	27	3.976	011
3.66	11	3.65	5	3.64	6	3.68	14	3.686	130
—		3.56	5	3.57	4	3.55	6	3.552	101
—		—		—		3.52	8	3.523	021
3.46	37	3.47	38	3.45	48	—			
—		—		—		3.39	44	3.389	200
3.27	18	3.26	10	3.26	6	3.29	100	3.294	040
3.17	73	3.13	34	3.14	39	3.12	38	3.126	121
3.11	100	3.11	100	3.11	78	3.01	45	3.014	220
3.02	11	2.75	50	2.76	57	2.76	50	2.762	131
2.76	51	2.66	3	—		2.68	89	2.683	230
—		2.60	3	2.62	6	2.63	16	2.635	050
—		—		—		2.58	10	2.579	211
								2.585	041
2.48	26	2.48	20	2.49	27	—			
—		—		2.44	9	2.45	10	2.456	150
2.41	11	2.41	4	2.40	9	2.41	4	2.415	141
—		2.36	4	2.34	6	2.36	6	2.362	240
2.25	15	—		—		2.26	6	2.260	300
2.24	15	2.24	10	2.24	12	2.23	21	2.227	310
2.20	26	2.19	24	2.18	24	2.11	13	2.116	151
2.11	22	2.11	16	2.10	18	2.09	20	2.089	160
2.06	33	2.06	20	2.05	21	2.06	16	2.059	012
—		2.05	20	—		2.00	16	2.009	330
1.97	29	—		—		1.98	4	1.987	301
1.96	24	1.97	22	1.96	27	1.96	6	1.965	311
—		—		—		1.90	13	1.902	321
—		—		—		1.88	4	1.884	032
1.85	7	1.85	6	1.86	9	1.86	4	1.863	340
1.83	18	1.82	10	1.82	12	1.84	4	1.861	251
—		—		1.79	8	1.81	8	1.815	132
—		—		1.76	6	1.76	3	1.760	212
1.73	18	1.72	10	1.71	9	1.71	6	1.715	222
								1.715	350
1.65	11	1.65	4	1.65	6	1.65	13	1.647	080
—		1.63	4	—		—		—	
1.58	11	1.57	5	1.57	9	1.58	7	1.586	351
								1.575	360
1.56	11	1.56	5	1.56	7	—		—	
1.50	11	1.50	6	1.52	8	—		—	
				1.50	6	—		—	
1.47	11	1.47	4	—		1.47	6	1.473	361

[a] This is mainly a β-HgClBr$_2$ pattern.
[b] Reflections of α-HgClBr$_2$.

TABLE II

X-Ray Powder Data for Reaction Product II

Reaction product II									
Prepared at 90°C		Heated to 120°C		Heated to 220°C		Heated to 250°C (α-HgClBr)			
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d_{calc}(Å)	hkl
5.98	21	5.98	14	—		—			
4.69	86	4.71	49	—		—			
4.50	86	4.52	84	4.49	100	4.50	100	4.505	120
4.15	46	4.15	28	4.13	65	4.17	55	4.166	011
3.94	21	3.94	21	—		—			
3.66	16	3.68	14	3.64	6	3.65	7	3.651	021
—		—		3.57	8	3.58	6	3.584	101
3.45	26	3.48	24	3.46	40	3.46	39	3.457	111
3.36	21	3.38	7	—		—			
3.24	46	3.28	21	3.26	8	3.28	11	3.281	040
—		3.15	56	3.15	24	3.15	33	3.145	121
3.11	100	3.11	100	3.11	71	3.11	67	3.100	031
3.01	21	3.01	14	—		—			
2.77	41	2.78	63	2.78	60	2.78	55	2.770	131
2.74	56	2.75	35	—		—			
2.61	16	2.62	14	—		—			
2.49	16	2.50	21	2.50	20	—			
—		—				2.49	25	2.486	211
—		—		2.41	8	2.42	6	2.420	141
				2.32	8	2.36	5	2.362	221
2.24	16	2.25	14	2.25	12	2.25	9	2.253	051
2.20	21	2.21	21	2.19	20	2.19	17	2.191	231
2.13	21	2.16	21	2.16	28	2.11	20	2.118	151
2.106	21	2.103	21	—		—		—	
2.074	21	2.056	24	2.06	40	2.05	18	2.045	112
2.047	21	—		—		—			
1.979	21	1.986	24	1.98	24	1.98	20	1.975	122
1.894	16	—		1.86	8	—			
1.823	16	1.83	14	1.83	16	1.83	18	1.825	042
1.800	16	—		—		—			
—		1.74	7	1.72	12	1.72	9	1.724	071
1.63	21	1.63	9	1.63	9	1.66	7	1.658	232
—		—		—		1.57	11	1.572	242
1.49	16	1.49	14	1.49	15	1.500	10	1.501	360

halogen molecules of $HgCl_2$ structure have been replaced by bromines, and since the radius of bromine atom is larger than that of chlorine, the lattice has expanded.

As a further study of the stability of α and β phases, reaction product I was recrystallized in alcohol, dried thoroughly and its X ray pattern was taken. It is observed that the β phase increased considerably with this treatment and the α phase decreased by almost the same amount. This indicates that when the product converts to a liquid-state (during crystallization) randomness in the distribution of Cl and Br atoms along
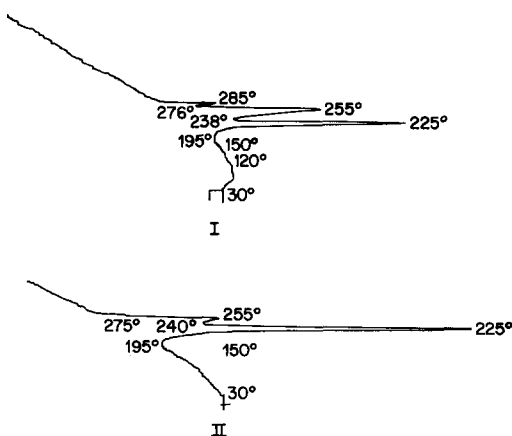
FIG. 1. (I) Product of Hg_2Cl_2 + $Br_2(g)$ reaction at 30°C. (II) Product of $HgCl_2$ + $HgBr_2(H)$ reaction at 90°C.

Hg in the halogen–Hg–halogen linkage increases and it remains so even after solidification. By heating below the melting point, the product being thus maintained in a solid state, the randomness in the molecular structure decreases and more of Cl and Br atoms get into the regular alternate arrangement along Hg linkages (α phase).

In the case of reaction II; i.e., between $HgCl_2$ (solid) and $HgBr_2$ (solid) the X-ray pattern of the product shows that the α and β phases are formed in almost equal amounts. Heating the product to 120°C gives a stronger pattern of α phase and a weaker one of β, and at 225°C only the α phase remains. It was not possible to get the β phase alone. However, its powder pattern could be indexed with the following cell parameters reported in literature for β-$Hg(ClBr)_2$ (3):

$$a = 6.78 \text{ Å}, b = 13.175 \text{ Å},$$
$$c = 4.17 \text{ Å}, Z = 4, \rho = 5.40$$

Therefore β-HgClBr also has a molecular structure similar to $HgCl_2$, with linear halogen–Hg–halogen molecules. The distribution of Cl and Br may be random in this case.

The mechanism of the reaction in both the cases seems to be a diffusion-controlled one. In solid-state reactions a relatively immobile product layer usually builds up at the initial point of contact between the reactants and the continued interaction depends on a diffusion mechanism by which the reacting species can pass through the product layers. So it appears to us that during bromination of Hg_2Cl_2 (reaction I) a product layer of α-HgClBr is built up as gaseous bromine comes into contact with Hg_2Cl_2. The reaction then proceeds by the continued interaction of bromine molecules with Hg_2Cl_2 molecules by diffusion through α-HgClBr.

Similarly in reaction II, $HgCl_2$ and $HgBr_2$ are initially in close contact with only a single phase-boundary separating them. Once the reaction starts a layer of the

TABLE III

X-Ray Powder Data for α-HgClBr and $HgCl_2$

α-HgClBr			$HgCl_2$		
d(Å)	I/I_0	hkl	d(Å)	I/I_0	hkl
4.50	100	120	4.365	100	120
4.16	56	011	4.107	40	011
3.65	7	021	3.587	7	021
3.58	6	101	3.511	5	101
3.46	39	111	3.386	10	111
3.28	11	040	3.192	12	040
3.15	33	031	3.038	30	031
3.11	67	200	2.989	50	200
2.78	55	131	2.708	40	131
2.49	25	211	2.418	20	211
2.42	6	141	2.361	4	141
2.35	5	221	2.295	3	221
2.25	9	051	2.199	8	051
2.19	17	231	2.13	14	231
2.11	20	151	2.065	16	151
2.05	18	112	2.012	10	112
1.98	20	122	1.941	14	122
1.83	18	042	1.793	10	042
1.72	9	071	1.681	3	071
1.66	7	232	1.621	4	232
1.57	11	242	1.537	5	242
1.50	10	360	1.454	4	360

product is formed between the two reactants and further contact between them is maintained by diffusion through the product layers. HgBr$_2$ molecules diffuse into HgCl$_2$ to give α-HgClBr. The counter diffusion of HgCl$_2$ into HgBr$_2$ gives β-HgClBr.

DTA curves of both the reaction products show endothermic reactions in the temperature region 195–240°C, 240–275°, and 275–290°C with peaks at 225, 255, and 285°C. These peaks differ in intensity in the two cases. The one at 225°C is stronger in product II than in I, whereas the other two are weaker. The peak at 225°C is attributed to the conversion of β phase to α. Since β phase is present in a lesser amount (as indicated by its weak X-ray pattern) in product I than in product II, therefore, less energy is consumed in conversion and hence a weaker maxima.

The existence of a peak at 255°C is attributed to the melting of α phase. This phase being present in a larger amount in product I, more energy is required to melt it which results in a stronger peak.

A peak at 285°C is obtained because sublimation is found to take place at this temperature. It is more intense in product I as the matter, which sublimates, is more in this case than in product II.

DTA studies thus support the findings obtained by X ray analysis.

It may be mentioned here that the X-ray data reported by Rastogi et al. (1), for reaction product I are not exactly similar to ours. Besides a few unidentified reflections,

their pattern seems to contain HgCl$_2$ reflections along with those of α-HgClBr and β-HgClBr. Hence their conclusion that the X-ray pattern obtained by them is of a single mixed halide, HgClBr, led them to incorrect cell parameters which they attribute as due to errors from X-ray absorption caused by the presence of heavy atoms.

It is interesting to know that the properties of mixed halides depend not only on the method of preparation but also on the order in which the anions were introduced into the molecule. This phenomenon has been named, in the case of mixed halides of quadrivalent platinum, as square coordination isomerism (2) since all of the differences are due to the fact that different halogens are found at different points of a square.

Acknowledgments

References

1. R. P. RASTOGI, B. L. DUBEY, AND N. D. AGRAWAL, J. Inorg. Nucl. Chem. 37, 1167 (1975).
2. S. S. BATSANOV, N. V. PODBEREZSKAYA, AND L. A. KHRIPIN, Zh. Neorg. Khim. 4, 1728 (1959).
3. W. SCHOLTEN AND J. M. BIJVOET, Z. Kristallogr. 103, 415 (1941).
4. ASTM Joint Committee for Powder Diffraction Systems, No. 26-315.