The Crystal Structure of Mercury (I) Bromate*

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The unit cell of mercury(I) bromate is monoclinic with the cell dimensions $a = 18.806$ Å, $b = 4.470$ Å, $c = 8.595$ Å, and $\beta = 107.19°$. The cell contains 4 formula units of $Hg_2(BrO_3)_2$. The space group is $C2/c$. The mercury atoms are linked in pairs across centres of symmetry, the Hg—Hg distance being 2.507 ± 6 Å. Each mercury atom has also a close oxygen neighbour at a distance of 2.16 ± 4 Å. The O—Hg—Hg—O group, thus formed, is nearly linear with the Hg—Hg—O angle $174 \pm 1°$. Two further oxygen atoms are situated 2.66 ± 6 Å and 2.69 ± 4 Å from the mercury atom.

Rather few crystal structures of mercury(I) compounds have been described in literature. This may seem somewhat astonishing in consideration of the peculiar character of monovalent mercury, which in all structures so far studied appears as doubly charged pairs of metal atoms. The geometrical shape and the electronic structure of this very simple kind of metal atom cluster is likely to give rise to rather interesting interaction with the structural environment in crystalline mercury(I) compounds. The present study of $Hg_2(BrO_3)_2$ is part of a research program comprising structural studies on inorganic and organic mercury(I) salts.[1] Investigations of the sulphate and selenate structures recently completed by the author will shortly be described elsewhere.

EXPERIMENTAL

The mercury(I) bromate used in this investigation was prepared from slightly acid mercury(I) nitrate solution and potassium bromate solution. Since the potassium bromate was not of *pro analysi* grade the first small precipitate, probably consisting of mercury(I) bromide was filtered off. The mercury bromate crystallized in about 20 min as colourless, very thin and six-sided plates. It was found possible to increase the thickness of the plates by evaporation of very dilute solutions. The single crystals used for the X-ray work were about 0.05 mm on an edge and 0.01 mm thick. There was no tendency of twinning and suitable rod-shaped single crystals could be cut parallel to the b-axis which runs along one of the plate edges.

Single crystal data were recorded with a Weissenberg camera using CuKα radiation. The crystal was rotated around the b-axis. However, the mercury(I) bromate was found

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* Structural Studies on Mercury(I) Compounds V.

to be rather unstable against X-ray radiation. The colour of the crystals changed from colourless to red in about 24 h of exposure. The product was not identified. It did not give any reflections in the Guinier powder photographs. It was therefore necessary to exchange the crystal for an unexposed one for every layer line photograph. Data were recorded for the reflections $h0l - h2l$ and the multiple film technique was used. A zero layer photograph with a crystal rotating around the c-axis was also recorded, but the weakness of the reflections hkl with k odd prevented any collecting of data of the odd layer lines around this axis. 196 independent reflections were recorded and the intensities measured visually by comparison with an intensity scale. The intensities obtained were corrected for absorption for each crystal, using a program written by Werner.[2]

The Weissenberg photographs showed monoclinic symmetry with the following extinctions: for reflections hkl when $h + k = 2n + 1$ and for reflections $h0l$ when $l = 2n + 1$. These conditions are characteristic of the space groups $C2/c$ (No. 15) and Cc (No. 9) of The International Tables. The cell constants obtained from a Guinier powder photograph were refined by a least squares method program written by Werner.[3] The cell dimensions are:

$$a = 18.806 \pm 7 \text{ Å}$$
$$b = 4.470 \pm 1 \text{ Å}$$
$$c = 8.595 \pm 2 \text{ Å}$$
$$\beta = 107.19 \pm 3°$$

The cell contents are 4 formula units of $Hg_2(BrO_3)_2$ the observed and calculated densities are 6.20 g/cm³ and 6.32 g/cm³, respectively.

The density of the compound was determined by the loss of weight in benzene.

A Patterson projection along [010] showed major peaks which could be interpreted as mercury-mercury and mercury-bromine vectors corresponding to atoms in general point positions of space group $C2/c$, i.e. 8(f): $(0,0,0;\frac{1}{2},\frac{1}{2},0)$ $\pm (x,y,z) \pm (x,\bar{y},\frac{1}{2}+z)$. (Since the assumption of this symmetry leads to a reasonable structure the other possible space group was not taken into consideration.) The x- and z-parameters were estimated from the Patterson projection as $x(\text{Hg}) = 0.065$, $z(\text{Hg}) = 0.985$, $x(\text{Br}) = 0.17$, and $z(\text{Br}) = 0.34$. Applying the signs of the structure factors obtained with this atomic arrangement a Fourier $\varrho (xz)$ map was calculated. This map showed clearly the mercury and bromine positions and some rather low peaks which could be interpreted as originating from oxygen atoms in general positions. To obtain more accurate oxygen parameters a Fourier map was calculated with the mercury and bromine atom contribution subtracted. The background was quite uniform and three peaks interpreted as due to oxygen atoms appeared at $0.17,y,0.45$ (O_1), $0.17,y,0.17$ (O_2) and $0.10,y,0.32$ (O_3).

A Patterson projection along [001] showed a major peak with $x = 0.13$ and a y-parameter around zero. This was interpreted as overlapping mercury-mercury vectors originating from the general position, i.e. $(2x,2y)$, $(2x,0)$, and $(2x,2\bar{y})$ and the y-parameter for mercury was therefore regarded as being ≈ 0. The mercury-bromine peaks indicated an y-parameter around 0.5 for the bromine atom. Thus the electron density projection along [001] calculated with the signs obtained with these y-values did not give accurate parameters for the heavy atoms due to the overlapping of the atoms in (x,y,z) and $(x,\bar{y}\ \frac{1}{2}+z)$. On the other hand two of the light atom peaks were visible, i.e.

O_1 with $x = 0.17$ and O_3 with $x = 0.10$. The y-parameter was estimated to 0.18 and 0.65, respectively, and the third oxygen y-parameter was calculated so as to give a reasonable bromate group. The mercury y-parameter was tentatively chosen as 0.00 and the bromine parameter as 0.51 after which a least squares refinement including all atoms was carried out with the $h0l$, $h1l$, and $h2l$ data. The scale factors between the layer lines were also refined, and isotropic temperature factors applied. The reliability factor was then 0.10.

A difference Fourier map calculated with $F_{obs}-F_{calc}$ where F_{calc} included the contributions from all atoms indicated, however, the possibility of an anisotropic thermal vibration for the mercury atoms. A refinement was therefore carried out applying a full matrix least squares program, LALS,[4] allowing anisotropic temperature factors. In order to limit the number of parameters the light atoms were assumed to have isotropic thermal vibration and no mutual variation was allowed for the scale factors. This refinement did not give any major shifts in the positional parameters, all shifts came out less than 0.05 Å for the light atoms and 0.02 Å for the mercury atom. However, the standard deviations decreased by about 40 %, a fact which justifies the application of anisotropic temperature factors to obtain a more correct structure.

Table 1. Final parameters obtained refining with anisotropic temperature factors for Hg. The temperature factor expression used is $\exp-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{23}kl + b_{13}hl)$.

	x	y	z	B Å^2
8(f) Hg	0.0642 ± 2	0.969 ± 1	0.9866 ± 3	
8(f) Br	0.1738 ± 3	0.446 ± 3	0.3372 ± 7	2.4 ± 2
8(f) O_1	0.172 ± 2	0.131 ± 11	0.458 ± 5	2.4 ± 9
8(f) O_2	0.181 ± 2	0.282 ± 11	0.171 ± 4	1.3 ± 7
8(f) O_3	0.090 ± 3	0.590 ± 13	0.302 ± 6	4.3 ± 1.2

b_{ij} for Hg	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
	0.0023 ± 1	0.047 ± 5	0.0173 ± 5	0.004 ± 1	0.0066 ± 3	0.007 ± 3

Table 2. Analysis of the weighting scheme used in the refinement.

Interval Fobs	Number of reflections	$\overline{w\,\Delta^2}$ normalized	Interval $\sin\theta$	Number of reflections	$\overline{w\,\Delta^2}$ normalized
0 — 81	19	1.00	0 — 0.46	61	1.15
81 — 94	22	1.29	0.46 — 0.58	44	0.96
94 — 109	17	0.77	0.58 — 0.67	26	0.60
109 — 130	20	1.34	0.67 — 0.74	14	1.24
130 — 152	20	0.70	0.74 — 0.79	16	0.62
152 — 173	19	0.73	0.79 — 0.84	8	0.31
173 — 196	20	0.72	0.84 — 0.89	9	1.25
196 — 249	19	1.43	0.89 — 0.93	7	0.88
249 — 337	20	0.97	0.93 — 0.97	8	0.61
337 — 660	20	1.06	0.97 — 1.00	3	2.37

Table 3. Observed and calculated *F*-values.

h	k	l	$|F_{obs}|$	$|F_{calc}|$	h	k	l	$|F_{obs}|$	$|F_{calc}|$	h	k	l	$|F_{obs}|$	$|F_{calc}|$	h	k	l	$|F_{obs}|$	$|F_{calc}|$
14	0	−10	125	133	−4	0	2	116	87	−3	1	5	86	93	−5	2	2	379	351
16	0	−8	151	145	−6	0	2	508	485	−3	1	4	102	99	−12	2	4	116	114
16	0	−6	165	173	−8	0	2	446	451	−5	1	4	81	82	−10	2	4	173	164
20	0	−6	179	160	21	1	−6	94	83	−7	1	4	441	435	−16	2	6	98	102
14	0	−4	367	368	21	1	−4	109	99	−9	1	4	249	246	−14	2	6	119	117
16	0	−4	117	140	23	1	−4	93	85	−11	1	4	152	142	−12	2	6	149	153
22	0	−6	103	96	19	1	−4	97	89	−13	1	4	93	98	−16	2	8	94	110
22	0	−4	199	183	13	1	−2	282	288	−15	1	4	236	231	−10	2	5	75	78
14	0	−2	216	246	17	1	−2	193	166	−17	1	4	212	197	−8	2	4	148	148
16	0	−2	278	304	21	1	−2	169	146	−3	1	3	71	71	−6	2	3	102	105
24	0	−2	92	124	23	1	−2	84	81	−5	1	3	77	78	−4	2	2	89	78
4	0	0	145	168	7	1	0	363	403	−3	1	2	51	33	−2	2	1	196	182
6	0	0	94	119	9	1	0	197	202	−5	1	2	333	310	−14	2	8	86	99
8	0	0	597	638	11	1	0	233	199	−7	1	2	302	293	−8	2	5	150	137
10	0	0	196	215	13	1	0	130	135	−9	1	2	409	436	−6	2	4	307	268
12	0	0	207	201	15	1	0	276	274	−15	1	2	149	153	−8	2	6	178	186
16	0	0	242	225	17	1	0	89	79	−1	1	1	132	123	−6	2	5	107	104
18	0	0	152	147	11	1	1	97	112	−3	1	1	38	28	−8	2	8	101	113
14	0	2	249	212	3	1	1	170	177	−5	1	1	122	141	−6	2	6	126	116
10	0	2	333	339	17	1	2	161	155	−7	1	1	94	91	−4	2	6	175	177
8	0	2	194	200	15	1	2	143	139	−9	1	1	114	107	−2	2	2	94	94
6	0	2	236	261	9	1	2	260	279	−3	1	0	337	368	−4	2	5	96	76
2	0	2	660	604	7	1	2	384	387	−5	1	0	301	287	−6	2	8	139	135
10	0	4	100	88	3	1	2	79	95	8	2	2	130	150	−2	2	3	173	172
8	0	4	163	185	1	1	2	350	374	10	2	2	216	227	−4	2	6	135	128
6	0	4	194	210	−1	1	2	516	631	16	2	4	83	98	−6	2	10	81	67
4	0	4	172	157	17	1	4	90	85	14	2	2	148	137	−2	2	4	270	241
2	0	4	309	269	13	1	4	71	86	2	2	0	206	206	0	2	2	224	282
8	0	6	194	192	9	1	4	269	276	4	2	0	65	66	0	2	4	186	187
2	0	6	110	121	7	1	4	86	67	6	2	0	155	167	0	2	5	132	136
2	0	6	150	174	5	1	4	75	48	8	2	0	369	350	0	2	6	194	201
0	0	2	422	380	3	1	4	90	95	10	2	0	170	163	0	2	1	50	54
0	0	4	285	255	1	1	4	484	487	12	2	0	123	102	−2	2	8	123	117
0	0	6	362	340	−1	1	4	168	162	14	2	0	116	100	−2	2	−4	160	142
−6	0	10	110	119	−3	1	3	79	80	16	2	0	155	144	−2	2	−3	139	125
−6	0	8	195	203	−1	1	3	64	82	18	2	0	88	94	−2	2	−6	104	97
−8	0	8	131	135	11	1	6	94	115	20	2	0	43	56	−4	2	−5	126	104
−14	0	8	145	149	3	1	6	215	215	−20	2	1	60	73	−2	2	−2	356	392
−4	0	6	213	196	1	1	6	162	156	−12	2	1	133	144	−4	2	−4	162	155
−6	0	6	128	115	−3	1	6	97	100	−22	2	1	56	65	−8	2	−6	128	118
−8	0	6	312	317	7	1	8	71	74	−16	2	2	219	226	−5	2	−4	154	163
−12	0	6	257	239	−1	1	8	118	122	−14	2	2	182	184	−10	2	−6	83	66
−2	0	4	360	318	−5	1	8	50	158	−8	2	2	352	326	−4	2	−2	80	64
−4	0	4	179	171	−9	1	8	84	97	−4	2	1	178	182	−8	2	−4	166	162
−6	0	4	488	453	−13	1	8	180	181	−16	2	4	98	90	−8	2	−3	107	94
−8	0	4	259	238	−5	1	6	236	240	−22	2	4	126	131	−6	2	−3	107	91
−10	0	4	218	194	−7	1	6	291	291	−14	2	4	295	245	−5	2	−2	174	169
−12	0	4	104	119	−13	1	6	167	170	−20	2	6	88	101	−4	2	−1	135	144
−2	0	2	175	146	−15	1	6	254	262	−10	2	3	194	177	−6	2	−1	189	192

A refinement carried out in this manner will not give true temperature factors b_{ij} for the mercury atom, but the relation between b_{11} and b_{33} is obtained since the rotation axis when collecting the Weissenberg data is b. As expected, the *R*-factor also decreased, *viz.* to 0.075. Hughe's weighting function $w = 1/h^2|F_o, min|^2$ for $|F_o| \leq h|F_o, min|$ and $w = 1/|F_o|^2$ for $|F_o| \geq h|F_o, min|$ with the parameter h given the value 4 was used in the refinement. The weight analysis obtained in the last cycles is given in Table 2 and a comparison between observed and calculated structure factors in Table 3.

The final parameters and temperature factors are given in Table 1. The thermal displacement of the mercury atoms corresponding to the b_{ij}:s given in this table were calculated with the program ORFFE.[5] Fig. 2 showing the $Hg_2(BrO_3)_2$ molecule was originally plotted by means of the program ORTEP[6] but the size of the oxygen atoms has been normalized in order to give a less confusing picture. The molecule is drawn with the oxygen triangle parallel to the plane of the paper.

DESCRIPTION OF THE STRUCTURE

The crystal structure of $Hg_2(BrO_3)_2$ exhibits some features of interest, *viz.* the presence of mercury atom doublets, which form part of almost linear $O-Hg-Hg-O$ groups and the molecular character of the structure. The mercury atom doublets are arranged almost parallel to the a-axis. The bond distance within the doublet is 2.507 ± 6 Å. Neighbouring doublets are around 4.5 Å apart, see Fig. 1. The $Hg-O_1$ distance in the chain $O_1-Hg-Hg-O_1$ is 2.16 ± 4 Å. Moreover, there are two short distances $Hg-O_3$ and $Hg-O_2'$, one to the same and one to a neighbouring bromate group -2.69 Å and 2.66 Å, respectively — making the coordination figure around the mercury atom a very distorted tetrahedron. The difference in the bonding forces points to a structure constructed from $Hg_2(BrO_3)_2$ molecules. These molecules, thus connected only by the weak $Hg-O_2'$ interaction, form linear chains along the c-axis. The influence of the mercury atom on the bromate group is indicated by an increase of the bonding distance $Br-O$ for the oxygen forming the nearly linear bond $Hg-Hg-O$. This $Br-O$ distance is 1.76 Å while the other two are 1.64 Å and 1.65 Å. Since the standard deviations for these bonding distances are $0.04-0.05$ Å the significance level, however, is only 95 %.

O = Hg   O = Br   O = O

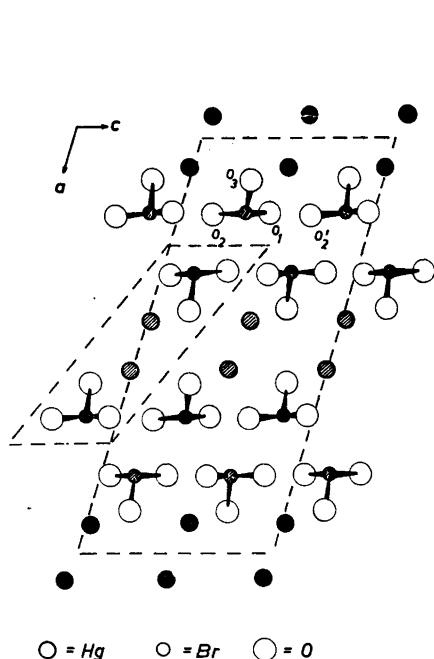*Fig. 1.* The structure of $Hg_2(BrO_3)_2$ projected along [010]. Hatched atoms are situated approximately in the plane $y = 0.5$, black atoms around the plane $y = 0$. The $Hg_2(BrO_3)_2$ molecule shown in Fig. 2 is outlined with dashed lines.
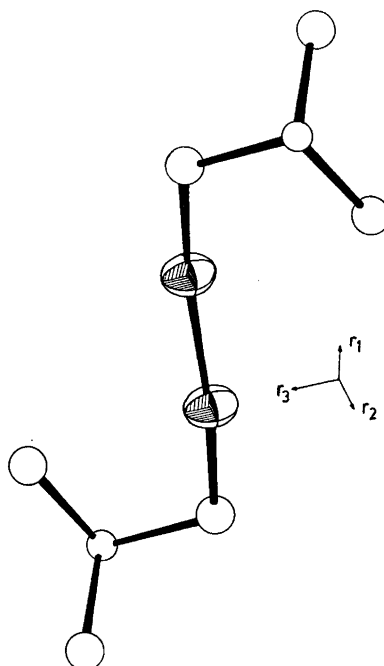
Fig. 2. The $Hg_2(BrO_3)_2$ molecule outlined in Fig. 1. The oxygen atom triangle is parallel to the plane of the paper.

Table 4. Interatomic distances and angles calculated with parameters shown in Table 1.

Distances, Å

	Hg	O_1	O_2	O_3
Hg	2.507 ± 6	2.16 ± 4	2.69 ± 4	2.66 ± 6
Br	3.30 ± 1	1.76 ± 5	1.65 ± 4	1.64 ± 5
O_1	—	2.99 ± 9	$\begin{cases} 2.61 \pm 6 \\ 2.57 \pm 6 \end{cases}$	2.68 ± 7
O_2	—	—	3.39 ± 5	2.69 ± 7
O_3	—	—	—	3.24 ± 10

Angles, degrees

$Hg-Hg-O_1$	$Hg-Hg-O_2$	$Hg-Hg-O_3$
174 ± 1	122 ± 1	109 ± 1
O_1-Br-O_2	O_1-Br-O_3	O_2-Br-O_3
100 ± 2	104 ± 2	110 ± 2
$O_1-O_2-O_3$	$O_2-O_3-O_1$	$O_3-O_1-O_2$
61 ± 2	58 ± 2	61 ± 2

RMS displacement for Hg (Å)

r_1	r_2	r_3
0.168 ± 8	0.21 ± 1	0.254 ± 9

The bromate groups are located so that the bromine atom apex is turned towards the oxygen atoms of the adjacent chain of $Hg_2(BrO_3)_2$ molecules. The distance to the closest oxygen atom $-O_1-$ is 2.93 ± 4 Å which is less than the sum of the van der Waals radii, -3.3 Å. These interactions seem to be the only forces holding the molecule chains together.

The thermal vibration of the mercury atom calculated with the b_{ij}:s obtained in the refinement mentioned before is more pronounced in directions perpendicular to the $O-Hg-Hg-O$ chain than along the bonds. This is at least true for vibration in planes parallel to the xz plane and — since the structural features are similar in the y- and z-directions — probably also for vibration in planes parallel to the xy-plane. Table 4 shows the interatomic distances and the RMS components of thermal displacement for mercury.

DISCUSSION

The reported interionic distances of the Hg_2^{2+} doublet varies from 2.43 Å in Hg_2F_2[7] to 2.69 Å in Hg_2I_2.[8] The structures of the two compounds $Hg_2(NO_3)_2 \cdot 2H_2O$[9] and $Hg_2(ClO_4)_2 \cdot 4H_2O$[10] containing linear $H_2O-Hg-Hg-OH_2$ groups have also been reported, both with approximately the same Hg—Hg distance, 2.54 ± 1 Å and 2.50 ± 1 Å, respectively. The mercury-mercury bonding distance in the present structure is close to these values and in agreement with recent investigations on the sulphate and selenate structure[11] and also with the distance found in Hg(I) o-phthalate.[12] All these compounds show the linear $O-Hg-Hg-O$ chain. Thus the strength of the Hg—Hg

bond may be regarded to be independent of the anion as long as there exists an Hg—O bond either to an oxygen of the anion or to a water molecule.

The angle, 174°, in the O—Hg—Hg—O chain and the Hg—O distance, 2.16 Å, indicates the covalent character of this bond. Within standard deviations this distance is the same as those found in the structures mentioned above and does not seem to be influenced by other atoms in the anion. However, the accuracy of the oxygen parameters in the nitrate and perchlorate is rather low and the similarity in distances may be an accidental occurrence.

The number of next nearest neighbours is very different in the Hg(I) compound structures so far determined. There are 3 (+ 2) in the perchlorate structure, 4 in the halogenides, 3 in the sulphate and selenate, and 2 in the nitrate and in the present structure. The bond lengths range from 2.4 Å to 3.0 Å and the arrangement around the mercury atom seems to be dependent both on the number of available atoms and the charge of these atoms. Thus there is little reason to assign to the mercury atom any other coordination number than 2.

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