

The Crystal Structure of $\text{Hg}(\text{OH})\text{BrO}_3$

GERT BJÖRNLUND

*Chemical Center, Divisions of Inorganic Chemistry, University of Lund, P.O.B. 740, S-220 07
Lund 7, Sweden*

The crystal structure of $\text{Hg}(\text{OH})\text{BrO}_3$ has been determined from X-ray single-crystal data. The crystals are orthorhombic, space group $Pbcm$, with four formula units per unit cell with the dimensions $a = 4.6467$, $b = 11.6482$, and $c = 7.2690$ Å.

The structure is built up of infinite nearly planar zig-zag $[\text{Hg}(\text{OH})]_n^{n+}$ chains and BrO_3^- ions. The former are similar to the $-\text{O}-\text{Hg}-\text{O}-$ chains of orthorhombic mercury(II) oxide.^{1,2} The $\text{Hg}-\text{O}$ distances in the present chains (2.07 Å) and the $\text{O}-\text{Hg}-\text{O}$ angles (175°) indicate that the bonds between these atoms are mainly sp or sd_z^2 in character. The value of the angle $\text{Hg}-\text{O}-\text{Hg}$ (123°) deviates from that of 107° found in orthorhombic HgO . The deformations of the chains are probably due to the influence of the bromate ions. These ions, forming pyramids, are situated between the infinite chains.

In connection with studies on the crystal chemistry of inorganic mercury(II) compounds, being performed at the Divisions of Inorganic Chemistry, University of Lund, it was found of interest to carry out a renewed investigation of the crystal structure of $\text{Hg}(\text{OH})\text{BrO}_3$, as an extremely short oxygen-oxygen distance of 1.78 Å was reported to exist in the compound.³ The earlier structure determination was based on a rather limited intensity material without any corrections for absorption.

EXPERIMENTAL

Preparation and analysis. Single crystals of $\text{Hg}(\text{OH})\text{BrO}_3$ were formed when solid potassium bromate was added to a hot 0.2 M mercury(II) nitrate solution.⁴ The transparent crystals have an octahedral shape with two opposite apexes cut off. The homogeneity of the samples was checked by X-ray Guinier-Hägg photographs.

The material thus prepared was analysed for mercury and bromate by conventional methods.^{5,6} The water analysis was made according to a modification of the method of Fischer.^{7,8} The results of the analyses were in good agreement with the values calculated for $\text{Hg}(\text{OH})\text{BrO}_3$. (Found: mercury 58.0; bromate 37.1; water 2.6. Calc.: mercury 58.1; bromate 36.1; water 2.6.)

Cell dimensions and density. The powder photographs were taken in a Guinier-Hägg focusing camera using $\text{CuK}\alpha_1$ radiation and potassium chloride as an internal standard.

Table 1. X-Ray powder data for $\text{Hg}(\text{OH})\text{BrO}_3$.

$h k l$	$10^5 \sin^2\theta_{\text{obs}}$	$10^5 \sin^2\theta_{\text{calc}}$	I_{obs}
0 2 0	1744	1749	st
1 0 0	2744	2748	st
0 2 1	2862	2872	m
1 1 0	3178	3185	st
0 0 2		4491	
1 2 0	4497	4497	vst
1 2 1	5615	5620	m
0 2 2	6240	6240	vst
1 3 0	6678	6683	w
0 4 0	6997	6996	m
1 0 2	7235	7239	vst
1 1 2	7667	7676	w
0 4 1	8114	8119	m
1 2 2	8981	8988	st
1 4 0	9737	9744	m
1 4 1	10858	10867	vw
2 0 0	10980	10991	m
1 3 2	11165	11174	w
2 1 0	11423	11428	st
2 2 0	12731	12740	vw
1 5 0	13687	13679	vw
2 2 1	13859	13863	vw
1 4 2	14235	14235	vst
2 3 0	14936	14926	vw
2 0 2	15486	15482	vw
0 6 0	15736	15742	w
2 1 2	15923	15919	m
0 6 1	16874	16864	vw
0 4 3	17104	17102	vw
2 2 2	17233	17231	st
1 6 0	18496	18489	vw
2 4 1	19131	19110	vw
2 3 2	19419	19417	m
0 2 4	19707	19714	w
1 4 3	19869	19849	vw
0 6 2	20237	20233	m
1 0 4	20717	20713	vw
1 1 4	21151	21150	vw
2 5 0	21921	21922	vw
1 2 4		22462	
2 4 2	22457	22478	vst
1 6 2	22958	22981	m

The powder pattern (Table 1) could be interpreted in terms of an orthorhombic unit cell with the following lattice parameters, with standard deviations in brackets:

$$\begin{aligned}
 a &= 4.6467 \text{ (6) } \text{Å} \\
 b &= 11.6482 \text{ (12) } \text{Å} \\
 c &= 7.2690 \text{ (9) } \text{Å}
 \end{aligned}$$

The volume of the unit cell is $393.44 \text{ (8) } \text{Å}^3$.

The density of the crystals, 5.76 g cm^{-3} , was determined from the apparent loss of weight in benzene, and indicated a cell content of four formula units $\text{Hg}(\text{OH})\text{BrO}_3$. The calculated density is 5.83 g cm^{-3} . These results are in good agreement with those previously reported.³

Single crystal intensity data. A single crystal of the approximate dimensions $0.06 \times 0.08 \times 0.14$ mm³, mounted along the *c*-axis, was used for recording the layers *hk0* – *hk4*, *hk6* and *hk8* (294 independent reflections) with an integrating Weissenberg camera, using Zr-filtered MoK α radiation. The layers *hk5* and *hk7* are missing for intensity reasons (p. 1648). The multi-film technique (three films) was used with thin steel foils between the films. The intensities of the reflections were measured by means of a microdensitometer and corrected for Lorentz and polarisation effects in the usual way. As the linear absorption coefficient μ was calculated to be 502.4 cm⁻¹, an absorption correction was carried out, the crystal being described by means of seven planes.

Computer programs. The digital computer CD 3600 of the *Computer Division of the National Swedish Rationalization Agency* in Uppsala was used for the calculations. The crystallographic data programs used are listed in Table 2.

Table 2. Computer programs.

Program	Subject	Authors
PIRUM	Least-squares refinement of unit cell parameters.	Werner, P.-E., Stockholm, Sweden. ¹³
DRF	Lorentz and polarization factors, Fourier summation.	Zalkin, A., Berkeley, USA. Modified by Liminga, R. and Lundgren, J.-O., Uppsala, Sweden.
DATAP2	Absorption corrections.	Coppens, P., Leiserowitz, L. and Rabinowich, D., USA. Revised by Olofsson, O. and Elfström, M., Uppsala, Sweden.
LALS	Full-matrix least-squares refinement of crystal structure parameters.	Gantzel, P., Sparks, R. and Trueblood, K., USA. Modified by Zalkin, A., Berkeley, USA, and by Liminga, R., Lundgren, J.-O. and Brändén, C.-I., Uppsala, Sweden. ¹⁴
ORFFE	A function and error program.	Busing, W. R., Martin, K. O. and Levy, H. A., Oak Ridge, USA. ¹⁵
DISTAN	Interatomic distances and angles.	Zalkin, A., Berkeley, USA.
ORTEP	A thermal-ellipsoid plot program.	Johnson, C., Oak Ridge, USA. ¹⁶

DETERMINATION OF THE CRYSTAL STRUCTURE

Space group. In the Weissenberg photographs, the reflections with the following indices were systematically missing: *0kl*, *k* odd; *h0l*, *l* odd. This is characteristic for the space groups *Pbc2*₁* and *Pbcm*.

The mercury and bromine atoms. The Patterson projection, *P(uvp)*, was calculated based on the reflections *hk0*. The peaks found in the projection

* Orientation different from *Pca2*₁ given in the *International Tables*.

could be interpreted by four-fold point positions both in $Pbc2_1$ and $Pbcm$. The following positional parameters were found for the mercury and the bromine atoms:

Hg: $x=0.060$, $y=0.250$; Br: $x=0.500$, $y=0.050$. If space group $Pbcm$ is the proper one, the four mercury atoms must be situated in one of the two special point positions $4(c)$: $\pm(x, \frac{1}{4}, 0)$, $\pm(x, \frac{1}{4}, \frac{1}{2})$; or $4(d)$: $\pm(x, y, \frac{1}{4})$, $\pm(\bar{x}, \frac{1}{2} + y, \frac{1}{4})$. As seen from the y -parameter, the four bromine atoms must be situated in $4(d)$. That $4(d)$ is not suitable for the mercury atoms will be seen below. Space group $Pbc2_1$ gives only one possibility, *viz.* the general point position $4(a)$.

The least-squares refinement of the parameters of the mercury atoms deduced in this way was then performed according to both $Pbc2_1$ and $Pbcm$. A zero value was assigned to the z -coordinate, as there are no symmetry conditions limiting the choice of the origin along this axis. When using $Pbc2_1$, the refinement was started a bit out of the position $y = \frac{1}{4}$. As the resulting standard deviation in the y -parameter was extremely large and as the value oscillated about $\frac{1}{4}$ from shift to shift, space group $Pbc2_1$ was considered to be less probable. On using $Pbcm$ during the refinement of the parameters for mercury and bromine in point positions $4(c)$ and $4(d)$, the shifts in the parameters converged normally, and the standard deviations were normally small. The discrepancy factor $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, based on the entire intensity material, was for $Pbcm$ 0.138 before, and 0.126 after correction for absorption.

The positions of the heavy mercury atoms led to the absence of the reflections $hk5$ and $hk7$, and the weakness of $hk1$ and $hk3$. For odd zones, there are namely no mercury contributions to the intensities.

The oxygen atoms. In order to find the oxygen atom positions, three-dimensional electron density difference syntheses were computed at different z -values, with the contributions of the mercury and the bromine atoms subtracted. All the maxima could be explained either as oxygen atoms or as residual peaks in the vicinity of the subtracted heavy atoms due to the use of scale factors not including the contributions of the oxygen atoms. The following oxygen atom positions were found ($Pbcm$):

	x	y	z
4 O1 in $4(d)$:	0.060	0.340	$\frac{1}{4}$
4 O2 in $4(d)$:	0.136	0.054	$\frac{1}{4}$
8 O3 in $8(e)$:	0.424	0.635	0.082

Refinement of the structure. The positional parameters of all the atoms, except hydrogen, the isotropic temperature factors, and the inter-layer scale factors, were refined using a full-matrix least-squares program. The refinement was considered to be complete when the shifts in the parameters were below 5 % of their standard deviations. The R -value was at that point 0.110.

Anisotropic temperature factors for the mercury and bromine atoms were then introduced. The isotropic temperature factors for the oxygen atoms were not converted to anisotropic ones because of the limited number of observed reflections. A new refinement was then performed, using an overall scale factor, obtained by fixing the inter-layer scale factors to the values found in the last cycle of the preceding refinement. The resulting R -value was 0.091. The quantity minimized was $w(|F_o| - |F_c|)^2$ with weighting according to

$w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$, $a = 200.0$, $c = 0.0015$, and $d = 0.0005$. The atomic scattering factors used for the neutral mercury were those given by Cromer and Waber,¹¹ and those for bromine and oxygen by Hanson *et al.*¹² The final parameters and their standard deviations are presented in Table 3, and the observed and calculated structure factors in Table 4. The weighting scheme is given in Table 5.

Table 3. The final parameters and standard deviations (in brackets). The temperature factor expression used for the mercury and the bromine atoms is $\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$. For mercury $\beta_{12} = \beta_{13} = 0$, and for bromine $\beta_{13} = \beta_{23} = 0$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)		
Hg	0.0631 (4)	$\frac{1}{4}$	0			
Br	0.5038 (13)	0.0518 (5)	$\frac{1}{4}$			
O1	0.082 (9)	0.334 (4)	$\frac{1}{4}$	2.8 (8)		
O2	0.154 (10)	0.052 (4)	$\frac{1}{4}$	2.9 (8)		
O3	0.417 (6)	0.631 (3)	0.079 (7)	3.0 (6)		

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	0.0207 (8)	0.0047 (2)	0.0099 (3)	0	0	0.0000 (10)
Br	0.0159 (17)	0.0042 (4)	0.0111 (11)	0.0035 (13)	0	0

The root-mean-square components of the thermal vibrations along the principal axes of the ellipsoids of the mercury and bromine atoms were calculated and are given in Table 6.

The hydrogen atoms. It has not been possible to locate the hydrogen atoms from the present intensity material. From the structure determination it is quite obvious that the formula of the compound is not HgO·Hg(BrO₃)₂·H₂O, but as mentioned above Hg(OH)BrO₃. It seems reasonable to assume that the hydrogen atoms are bonded to the non-bromate oxygen atoms, since otherwise the compound would have the chemical formula HgO·HBrO₃, which is very unlikely. Starting from this assumption concerning the formula, more detailed discussion of the positions of the hydrogen atoms and of the possible occurrence of hydrogen bonding in the structure is given below.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

It has been assumed above that the hydrogen atom does not belong to the bromate oxygen atom. Thus it must be associated to the basic oxygen atom O1, and consequently the structure is assumed to be built up of infinite zig-zag $[-(\text{OH})-\text{Hg}-(\text{OH})-]_n^{n+}$ chains and separate bromate ions. Experiments to exchange the OH⁻ ions for F⁻ ions are in progress in order to investigate whether or not hydrogen bonding plays an important role in the

Table 4. Observed and calculated structure factors for $\text{Hg}(\text{OH})\text{BrO}_3$. The columns give in order $h, k, l, |F_o|, |F_c|$.

0	2	0	231	194	-1	2	1	93	100	-5	9	2	60	54	0	6	6	101	104
0	4	0	255	241	-1	4	1	64	69	-6	0	2	72	87	0	8	6	119	125
0	6	0	222	232	-1	6	1	66	58						0	10	6	50	41
0	8	0	113	117	-1	8	1	43	41	0	4	3	117	115	0	12	6	75	77
0	10	0	185	199	-2	1	1	26	22	0	6	3	94	99	0	14	6	53	41
0	12	0	59	62	-2	2	1	53	55	-1	2	3	38	34	-1	0	6	218	187
0	14	0	86	73	-2	4	1	76	83	-1	4	3	57	64	-1	1	6	49	55
0	16	0	68	60	-2	6	1	46	59	-1	6	3	70	76	-1	2	6	77	87
-1	0	0	202	139	-2	8	1	35	27	-2	2	3	37	27	-1	3	6	46	51
-1	1	0	119	111	-3	2	1	62	53	-2	4	3	69	72	-1	4	6	114	123
-1	2	0	274	352	-3	4	1	72	76	-2	6	3	57	63	-1	5	6	42	41
-1	3	0	90	104	-3	6	1	56	63	-3	2	3	50	45	-1	6	6	118	120
-1	4	0	191	236	-3	8	1	23	29	-3	4	3	65	64	-1	7	6	45	46
-1	5	0	94	107	-4	1	1	30	32	-1	6	3	54	54	-1	8	6	71	65
-1	6	0	148	155	-4	4	1	47	47	-4	2	3	42	36	-1	10	6	95	95
-1	8	0	195	184	-4	6	1	44	44	-4	4	3	46	40	-2	0	6	46	35
-1	9	0	60	52	-5	2	1	22	21	-4	6	3	37	33	-2	1	6	96	77
-1	10	0	78	67	-5	4	1	45	43	-5	2	3	36	26	-2	2	6	134	122
-1	11	0	36	40	-5	6	1	39	36						-2	3	6	96	98
-1	12	0	129	123						0	2	4	156	137	-2	4	6	80	76
-1	13	0	45	34	0	4	2	219	196	0	4	4	224	212	-2	5	6	80	81
-1	14	0	72	61	0	6	2	180	174	0	6	4	177	179	-2	6	6	51	60
-2	0	0	319	299	0	8	2	229	230	0	8	4	77	72	-2	7	6	60	69
-2	1	0	234	226	0	10	2	55	66	0	10	4	134	148	-2	8	6	82	84
-2	2	0	105	100	-12	2	2	105	115	0	12	4	42	58	-2	9	6	41	51
-2	3	0	122	127	-1	0	2	406	301	0	14	4	61	61	-3	0	6	104	86
-2	4	0	155	153	-1	1	2	89	79	-1	0	4	170	137	-3	1	6	123	103
-2	5	0	113	129	-1	2	2	149	151	-1	1	4	87	90	-3	3	6	111	88
-2	6	0	125	145	-1	3	2	105	111	-1	2	4	237	244	-3	4	6	45	47
-2	7	0	101	111	-1	4	2	241	255	-1	3	4	62	64	-3	5	6	84	85
-2	8	0	57	59	-1	5	2	86	84	-1	4	4	139	136	-3	6	6	42	45
-2	9	0	101	100	-1	6	2	214	215	-1	5	4	65	63	-3	7	6	74	79
-2	10	0	135	128	-1	7	2	75	74	-1	6	4	107	112	-3	9	6	57	64
-2	11	0	80	77	-1	8	2	92	88	-1	7	4	61	48	-3	11	6	53	47
-3	1	0	185	172	-1	9	2	43	46	-1	8	4	161	157	-4	0	6	27	29
-3	2	0	155	141	-1	10	2	149	149	-1	9	4	45	47	-4	1	6	86	80
-3	3	0	176	185	-1	11	2	37	36	-1	10	4	56	58	-4	3	6	98	87
-3	4	0	43	43	-1	12	2	55	50	-1	12	4	85	90	-4	5	6	92	79
-3	5	0	142	153	-2	0	2	91	73	-1	14	4	41	47	-4	7	6	63	64
-3	7	0	106	113	-2	1	2	194	152	-2	0	4	261	194	-4	9	6	47	53
-3	8	0	49	93	-2	2	2	238	217	-2	1	4	167	134	-5	1	6	61	63
-3	9	0	86	97	-2	3	2	155	157	-2	2	4	84	72	-5	2	6	57	45
-3	11	0	62	79	-2	4	2	110	115	-2	3	4	115	113	-5	3	6	37	52
-3	12	0	57	51	-2	5	2	108	117	-2	4	4	122	128	-5	5	6	59	56
-3	13	0	72	67	-2	6	2	115	96	-2	5	4	100	114	-5	7	6	36	46
-4	0	0	46	45	-2	7	2	143	147	-2	6	4	103	113	-6	0	6	52	52
-4	1	0	154	163	-2	8	2	143	147	-2	7	4	75	74					
-4	2	0	54	49	-2	9	2	91	93	-2	9	4	70	68	0	2	8	54	60
-4	3	0	136	131	-2	11	2	64	57	-2	10	4	97	97	0	4	8	67	98
-4	5	0	111	115	-2	12	2	81	76	-2	11	4	64	63	0	6	8	72	86
-4	7	0	103	109	-3	0	2	171	151	-3	1	4	170	145	0	10	8	74	72
-4	9	0	84	88	-3	1	2	177	152	-3	2	4	125	105	-1	0	8	69	62
-4	11	0	66	73	-3	3	2	176	160	-3	3	4	139	129	-1	1	8	40	44
-4	13	0	37	47	-3	4	2	83	80	-3	5	4	115	105	-1	2	8	96	110
-5	0	0	91	87	-3	5	2	147	156	-3	7	4	87	96	-1	3	8	26	31
-5	1	0	99	95	-3	6	2	69	70	-3	8	4	77	72	-1	4	8	61	65
-5	3	0	101	106	-3	7	2	116	121	-3	9	4	79	85	-1	6	8	58	56
-5	4	0	62	55	-3	9	2	85	87	-3	11	4	52	61	-1	8	8	77	77
-5	5	0	83	79	-3	10	2	64	75	-4	0	4	45	41	-2	0	8	111	86
-5	6	0	55	47	-3	11	2	78	76	-4	1	4	135	116	-2	1	8	71	62
-5	7	0	71	74	-3	13	2	50	52	-4	2	4	41	37	-2	2	8	37	30
-5	9	0	73	62	-4	0	2	54	56	-4	3	4	127	109	-2	3	8	57	58
-5	10	0	55	49	-4	1	2	147	137	-4	5	4	102	99	-2	4	8	60	62
-5	11	0	51	43	-4	2	2	39	41	-4	7	4	89	83	-2	5	8	54	58
-6	1	0	56	50	-4	3	2	139	131	-4	9	4	67	65	-2	6	8	55	55
-6	2	0	81	85	-4	5	2	116	117	-4	11	4	66	60	-3	1	8	89	71
-6	3	0	40	47	-4	7	2	103	104	-5	0	4	80	75	-3	2	8	52	49
-7	0	0	36	72	-4	9	2	91	88	-5	1	4	64	79	-3	3	8	74	64
					-4	11	2	67	58	-5	3	4	86	82	-3	5	8	54	53
					-5	1	2	86	98	-5	5	4	65	61	-3	7	8	46	50
					-5	2	2	74	73	-5	7	4	51	61	-4	1	8	62	60
					-5	3	2	80	83	-6	2	4	54	67	-4	3	8	56	56
					-5	5	2	102	91						-5	5	8	60	52
					-5	7	2	72	66	0	2	6	191	188	-5	8	8	44	42
					-5	8	2	55	52	0	4	6	132	133	-5	3	8	46	43

structure. This is the first example known to the author of a structure with $[\text{Hg}(\text{OH})_n]^{n+}$ chains as a structural element. In the earlier work on this structure, these chains were also assumed to exist. The hydrogen atoms of the chains may form hydrogen bonds to one of the bromate oxygen atoms O2, since the closest distance O1-O2 is 2.77 (7) Å, which is a possible hydrogen bond distance. Hydrogen bonds of the type O-H...O vary normally between 2.5 and 2.8 Å.¹⁰ Thus if hydrogen bonding occurs in the structure, it must exist between the atoms O1 and O2, which is further supported by the fact that the angle Hg-O1-O2 is 114.8 (1.2)°, not far from the value for a tetra-

Table 5. The weighting scheme used in the last cycle of the refinement of the parameters for Hg(OH)BrO₃. The averages $w(|F_o| - |F_c|)^2 = w\Delta^2$ are normalized.

Interval $ F_o $	$\overline{w\Delta^2}$	No. of reflections	Interval $\sin\theta$	$\overline{w\Delta^2}$	No. of reflections
0.0 - 42.4	1.32	29	0.00 - 0.26	0.87	72
42.4 - 51.6	1.00	29	0.26 - 0.33	0.51	53
51.6 - 57.7	1.27	30	0.33 - 0.37	0.52	45
57.7 - 67.5	0.84	29	0.37 - 0.41	0.63	38
67.5 - 77.9	0.84	30	0.41 - 0.44	0.81	34
77.9 - 87.8	0.51	29	0.44 - 0.47	0.76	24
87.8 - 102.3	1.04	29	0.47 - 0.50	1.07	12
102.3 - 124.8	0.88	30	0.50 - 0.52	1.07	11
124.8 - 169.6	1.04	29	0.52 - 0.54	3.42	2
169.6 - 408.0	1.26	30	0.54 - 0.56	0.34	3

Table 6. Root-mean-square components R_i (Å), with standard deviations in brackets, calculated for the mercury and the bromine atoms from the β_{ij} -values given in Table 3.

	R_1	R_2	R_3
Hg	0.150 (3)	0.163 (3)	0.179 (3)
Br	0.125 (11)	0.172 (9)	0.174 (10)

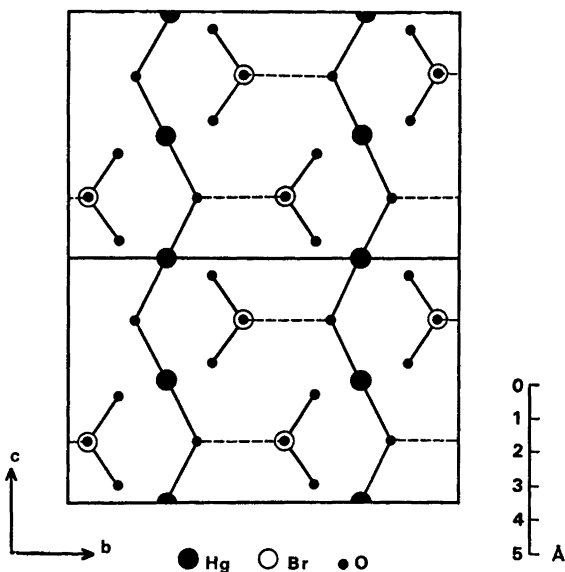


Fig. 1. A projection of two unit cells of the structure on the yz -plane. The hydrogen bonds are dotted, and the other bonds full lined. Each bromine atom is covered by or covering one oxygen atom in the picture.

hedral bond. The projection of two unit cells of the structure on the yz -plane is shown in Fig. 1. The chains $[\text{Hg}(\text{OH})]_n^{2+}$ almost run in a plane parallel to the yz -plane in the z -direction. The two $\text{Hg}-\text{O}1$ distances are found to be 2.07 (2) Å (the point symmetry of Hg is 2). The angles $\text{O}1-\text{Hg}-\text{O}1$ and $\text{Hg}-\text{O}1-\text{Hg}$ are 175.2 (2.3) $^\circ$ and 123.1 (2.2) $^\circ$, respectively. The distances $\text{Hg}-\text{O}1$ in the chains are in good agreement with those reported for other $-\text{O}-\text{Hg}-\text{O}-$ chains.²

The mercury atoms are, in addition to the oxygen atoms in the chains, surrounded by three other pairs oxygen atoms, belonging to the bromate groups, at distances of 2.69 (3), 2.84 (3) and 2.96 (4) Å, respectively. These six oxygen atoms are approximately situated in a plane almost perpendicular to that of the chain. From a geometrical point of view, the mercury atoms could very roughly be described as surrounded by distorted hexagonal bipyramids of oxygen atoms. The angle between the short axes of two consecutive bipyramids is 123.1 (2.2) $^\circ$ (the angle $\text{Hg}-\text{O}1-\text{Hg}$ of the chain). These bipyramids have one edge in common, which is illustrated in Fig. 2. Each of them also shares two other edges with those of the neighbouring cells in the a -direction.

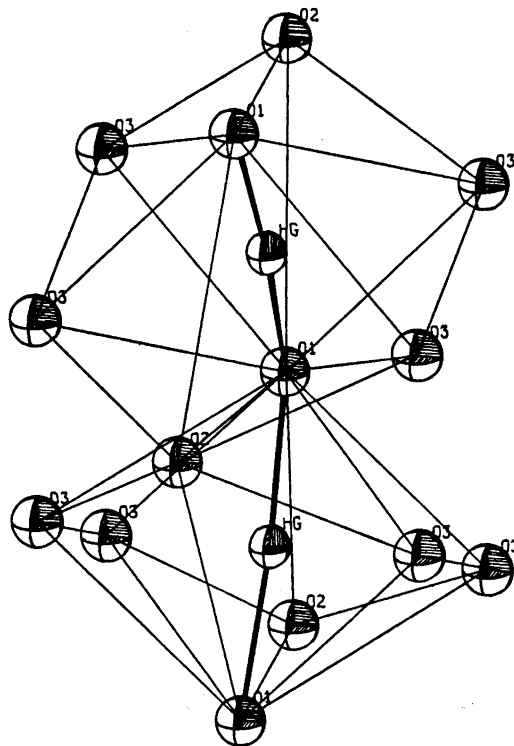


Fig. 2. The oxygen arrangement around two consecutive mercury atoms in the same $-(\text{OH})-\text{Hg}-(\text{OH})-$ chain.

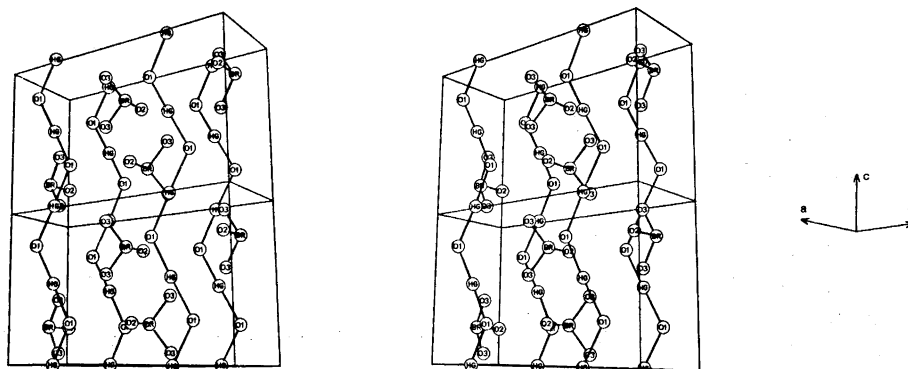


Fig. 3. A stereoscopic pair of drawings, showing the structure of $\text{Hg}(\text{OH})\text{BrO}_3$. The hydrogen atoms are omitted. In addition to two complete unit cells, two $-\text{O}-\text{Hg}-\text{O}-$ chains from neighbouring unit cells in the a -direction are also shown.

The bromate groups forming pyramids are situated in between the $[\text{Hg}(\text{OH})]_n^{n+}$ chains, as shown in Fig. 3. The $\text{Br}-\text{O}$ distances of the bromate group are in good agreement with those given in the literature.¹⁷

Table 7. Distances (\AA) and bond angles ($^\circ$) with standard deviations (in brackets) in $\text{Hg}(\text{OH})\text{BrO}_3$. The symbols used in Table 7, Fig. 2, and Fig. 3 are the same.

$\text{Hg}-2\text{O1}$	2.07 (2)
$\text{Hg}-2\text{O3}$	2.67 (3)
$\text{Hg}-2\text{O3}$	2.84 (3)
$\text{Hg}-2\text{O2}$	2.96 (4)
$\text{Br}-2\text{O3}$	1.59 (4)
$\text{Br}-\text{O2}$	1.63 (5)
$\text{O1}-\text{O2}$	2.77 (7)
$\angle\text{O1}-\text{Hg}-\text{O1}$	175.2 (2.3)
$\angle\text{Hg}-\text{O1}-\text{Hg}$	123.1 (2.2)
$\angle\text{O2}-\text{Br}-\text{O3}$	103.2 (1.5)
$\angle\text{O3}-\text{Br}-\text{O3}$	102.8 (2.9)
$\angle\text{Hg}-\text{O1}-\text{O2}$	114.8 (1.2)
$\angle\text{Br}-\text{O2}-\text{O1}$	113.0 (2.5)

Interatomic distances and angles of interest, with estimated standard deviations, are given in Table 7. It should be noted that the distance $\text{O1}-\text{O2}$, previously reported to be 1.78 \AA , was now found to be 2.77 (7) \AA .

Acknowledgements. The author wishes to thank Dr. Karin Aurivillius for her help in introducing him to the techniques of structure determination, her valuable discussions during this work and her stimulating and helpful interest. The author is also indebted to Professors Sture Fronæus and Bengt Aurivillius for their kind interest in this work.

The author is grateful to the *Computer Division of the National Swedish Rationalization Agency* for the use of the CD 3600 computer in Uppsala. This investigation is part of a research project, supported by the *Swedish Natural Science Research Council*.

REFERENCES

1. Aurivillius, K. *Arkiv Kemi* **18** (1964) 1305.
2. Aurivillius, K. *Arkiv Kemi* **24** (1965) 151.
3. Weiss, A., Lyng, S. and Weiss, A. *Z. Naturforsch.* **15b** (1960) 678.
4. Gmelin-Kraut, *Handbuch der anorganischen Chemie*, 7th Ed., Heidelberg 1914, Vol. V, p. 752.
5. Schwarzenbach, G. and Flaschka, H. *Die komplexometrische Titration*, 5th Ed., Ferdinand Enke Verlag, Stuttgart 1965, p. 215.
6. Vogel, A. I. *A Textbook of Quantitative Inorganic Analysis*, 3rd Ed., Longmans, London 1961, p. 385.
7. Vogel, A. I. *A Textbook of Quantitative Inorganic Analysis*, 3rd Ed., Longmans, London 1961, p. 944.
8. Karlsson, R. *Private communication*.
9. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 122.
10. Pauling, L. *The Nature of Chemical Bond*, 3rd Ed., Cornell University Press, New York 1960.
11. Cromer, D. T. and Waber, I. T. *Acta Cryst.* **18** (1965) 104.
12. Hanson, H. P., Herman, F., Lea, I. D. and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
13. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., 1966, No. 6027.
14. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., 1966, No. 384.
15. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., 1966, No. 363.
16. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., 1966, No. 387.
17. Wells, A. F. *Structural Inorganic Chemistry*, Clarendon Press, Oxford 1962, p. 333.

Received October 1, 1970.