This investigation was supported by Public Health Service Research Grant CA06183 from the National Chancer Institute.

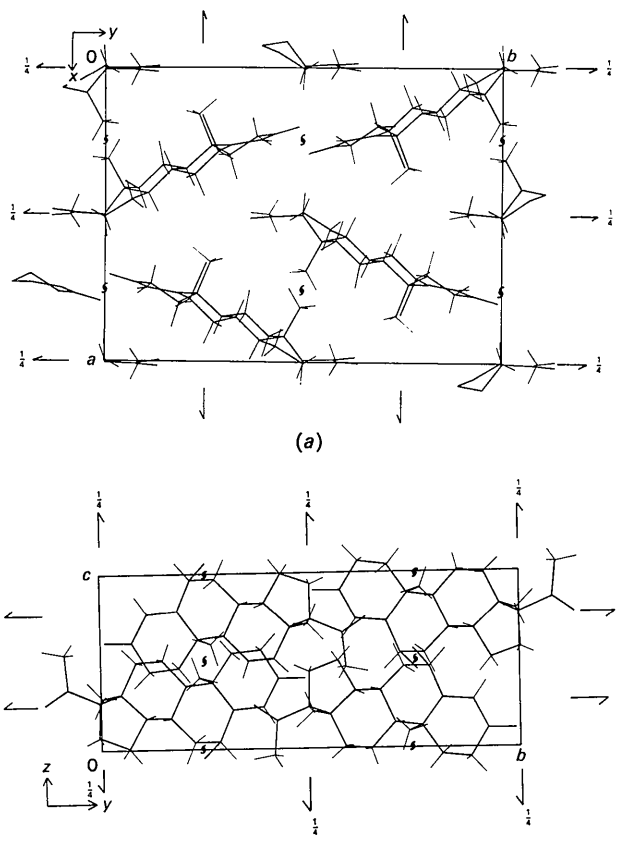

Fig. 4. Projection of one unit cell (*a*) onto the (001) plane and (*b*) onto the (100) plane.

Table 7. *Intermolecular contacts less than* 4·0 Å *between carbon and heavier atoms*

Atom 1	Atom 2	Position*	Distance
Br	C(1)	1/001	3·805 (5) Å
Br	C(2)	1/001	3·993 (5)
Br	C(20)	2/110	3·763 (5)
Br	C(21)	2/110	3·679 (5)
Br	O(20)	2/110	3·191 (4)
O(3)	C(2)	2/100	3·576 (6)
O(3)	C(4)	2/10$\bar{1}$	3·439 (6)
O(3)	C(17)	3/$\bar{1}$01	3·787 (8)
O(3)	C(20)	3/$\bar{1}$01	3·820 (6)
O(3)	C(21)	3/$\bar{1}$01	3·326 (6)
O(20)	C(19)	2/110	3·803 (6)
C(1)	C(6)	1/00$\bar{1}$	3·856 (7)
C(12)	C(15)	1/00$\bar{1}$	3·975 (7)

* Equivalent position nomenclature: 3/$\bar{1}$01 is taken to mean that the second atom mentioned in the intermolecular distance is at equivalent position 3, translated -1, 0 and 1 unit cells in the *a*, *b* and *c* directions respectively. The equivalent positions are $1=(x,y,z)$; $2=(\frac{1}{2}-x,\bar{y},\frac{1}{2}+z)$; $3=(\frac{1}{2}+x,\frac{1}{2}-y,\bar{z})$.

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The Crystal Structure of Potassium Mercuric Tribromide Monohydrate, $KHgBr_3 . H_2O$

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The crystal structure of potassium mercuric tribromide monohydrate has been determined by X-ray diffraction techniques. The structure consists of four molecules linked by hydrogen bonds and van der Waals forces, in a unit cell of $Cmc2_1$ symmetry, and of dimensions $a=4{\cdot}37$, $b=16{\cdot}87$ and $c=10{\cdot}14$ Å. The mercury atom is surrounded by four bromine atoms in an irregular tetrahedron. The bromine atoms at $x=\frac{1}{2}$ and $-\frac{1}{2}$ are shared, resulting in a zigzag chain of Br–Hg–Br–Hg atoms along the *a* axis. The other bromine atoms are held by hydrogen bonds of the water molecule.

Introduction

While making a survey of the literature for structures having hydrogen bonded bromine atoms, the authors became interested in the crystal structure of potassium mercuric tribromide monohydrate. Unit-cell dimensions were determined by Herak, Manojlivic & Malcis (1963) but no complete structure analysis has yet been

undertaken. In the present paper we report the crystal structure of the compound from three-dimensional X-ray diffraction data.

Experimental

Thin colourless plates of $KHgBr_3H_2O$ crystals are readily obtained by the method described by Herak *et al.* (1963). Unit-cell dimensions measured from high level Weissenberg spots are $a=4{\cdot}37\pm0{\cdot}01$, $b=16{\cdot}87\pm0{\cdot}02$ and $c=10{\cdot}14\pm0{\cdot}02$ Å. Systematic absences corresponded to the space groups $Cmc2_1$, $C2cm$ or $Cmcm$ with four molecules in the unit cell. The calculated density is 4·45 g.cm^{-3} and the density measured by flotation in mixed solvents was found to be 4·40 g.cm^{-3}. Intensities of about 280 $Okl, 1kl, 2kl, hK0, hK1$ and $hK2$ reflexions were measured with nickel filtered copper $K\alpha$ radiation on an equi-inclination Weissenberg camera, the standard multiple technique being used. The crystals were approximated to a cylinder, $\mu R=1{\cdot}30$ ($\mu=650$ cm^{-1}) and the data corrected for absorption accordingly. The visually estimated intensities were corrected for Lorentz–polarization and spot-size. The observed structure factors were put on an absolute scale with the help of Wilson's (1942) plot and were later adjusted during refinement.

Analysis of the structure

From ($hk0$) and ($0kl$) Patterson projections and spatial considerations, approximate positional parameters of the Hg atom and the Br atoms were obtained. An inspection of the film data showed that the reflexions hkl were very weak, when l was odd which can happen when the total contribution from the heavy atoms is small. Of the three space groups $Cmc2_1$, $Cmcm$, $C2cm$ this was found to be possible with $Cmc2_1$ and so this space group was assumed. Subsequent refinement verified this choice.

The Patterson projections showed that the mercury atom and all the bromine atoms are in fourfold positions, namely 4(a) $0yz$ *etc.* Taking the phase contribution from these atoms a Fourier synthesis was computed with limited $hk0$ reflexions. The projection did not give any specific information about the positions of the oxygen (water molecule) and the potassium atoms. So, from considerations of packing and interatomic distances, tentative coordinates were obtained for the oxygen and potassium atoms and refinement was started with these positions. Moving the oxygen and the potassium atoms gave the reliability factor $\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|=0{\cdot}28$, with reasonable thermal parameters for all the atoms (hydrogen atoms not included). Then four cycles of refinement using all the data, (each reflexion with weight $1/F_o$) with isotropic thermal parameters for each atom, was carried out on a CDC 3600 computer using the least-squares program of Busing, Martin & Levy (1962). The reliability factor at this stage was 0·15. Further refinement with individual anisotropic temperature factors was made and at the end of five cycles the R value converged to 0·10. In the final stages of refinement unit weight was given to all reflexions with $F_o>35$ and zero weight to reflexions with $F_o\leq35$. The scattering curves for Hg–Br (both corrected for dispersion), K and O used for the structure factor calculations have been taken from *International Tables for X-ray Crystallography* (1962). The atomic parameters are listed in Tables 1 and 2 and the structure factors in Table 3.

Table 1. *Atomic coordinates*

	x	y	z	$\sigma(y)$	$\sigma(z)$
Hg	0	0·001	0·248	0·001	0·001
Br(1)	0	0·132	0·099	0·001	0·001
Br(2)	0	−0·130	0·130	0·001	0·001
Br(3)	0	0·498	0·847	0·001	0·001
O(H_2O)	0	0·297	0·015	0·002	0·002
K	0	0·238	0·339	0·002	0·002

Table 2. *Anisotropic thermal parameters* ($\times10^4$) *and standard deviations*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	17 (5)	12 (2)	112 (11)	0	0	2 (3)
Br(1)	312 (22)	13 (1)	42 (4)	0	0	19 (4)
Br(2)	82 (7)	14 (2)	33 (2)	0	0	−16 (5)
Br(3)	138 (14)	20 (5)	120 (21)	0	0	30 (8)
O	310 (21)	56 (6)	185 (14)	0	0	17 (9)
K	213 (30)	12 (2)	212 (20)	0	0	−12 (3)

The definition of the Debye–Waller temperature factor is: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Discussion

The interatomic distances and bond angles are shown in Table 4. All the atoms lie in the mirror plane $x=0$ and the sheet structure (Figs. 1 and 2) can also be described in terms of coordination around the mercury atom. Divalent mercury compounds tend to form either two collinear bonds, presumably sp, or four tetrahedral bonds by sp^3 hybridization. In this structure the mercury atom has four bromine atoms at the corners of a distorted tetrahedron with the Hg–Br distance lying in the range 2·41–2·67 Å. These values can be compared with the reported values ranging from 2·25 to 2·92 Å (Wells, 1962). Two of these bromine atoms located at $x=\frac{1}{2}$ and $-\frac{1}{2}$ are shared by the tetrahedron of the adjacent cells, resulting in a zigzag chain of Hg–Br–Hg–Br atoms along a axis. The other two bromine atoms are bonded to the bromines of the neighbouring molecule by hydrogen atoms of the water molecule. The nature of the hydrogen bond involving the water molecule cannot be definitely established from the results of this analysis. From a consideration of interatomic distances there appear to be three bromine atoms at suitable distances (two at 2·77 Å and a third at 2·91 Å) to form hydrogen bonds. As there are only two protons available, it is possible that one of them forms a bifurcated hydrogen bond.

Table 3. *Observed and calculated structure factors*

H	K	L	F_{obs}	$\|F_{cal}\|$	H	K	L	F_{obs}	$\|F_{cal}\|$	H	K	L	F_{obs}	$\|F_{cal}\|$	H	K	L	F_{obs}	$\|F_{cal}\|$
0	2	0	272	286	0	2	3	27	24	1	3	5	37	47	2	6	6	108	114
0	4	0	221	229	0	4	3	28	12	1	5	5	32	34	2	8	6	57	62
0	6	0	478	490	0	6	3	26	28	1	7	5	27	22	2	10	6	170	160
0	8	0	468	483	0	8	3	27	35	1	9	5	32	28	2	12	6	122	130
0	10	0	135	127	0	10	3	54	44	1	11	5	30	27	2	14	6	96	101
0	12	0	151	156	0	12	3	26	24	1	1	6	303	301	2	2	7	32	33
0	14	0	262	280	0	14	3	26	26	1	3	6	198	166	2	4	7	22	10
0	16	0	192	213	0	2	4	196	202	1	5	6	187	173	2	6	7	37	39
0	18	0	35	34	0	4	4	280	294	1	7	6	152	150	2	8	7	37	28
0	20	0	122	126	0	6	4	109	131	1	9	6	178	171	2	10	7	30	30
1	1	0	292	306	0	8	4	122	129	1	11	6	135	143	2	2	8	118	112
1	3	0	38	43	0	10	4	237	227	1	13	6	122	136	2	4	8	106	110
1	5	0	43	51	0	12	4	124	156	1	1	7	37	32	2	6	8	110	95
1	7	0	310	308	0	14	4	125	133	1	3	7	49	38	2	2	9	37	37
1	9	0	132	143	0	2	5	37	27	1	5	7	33	28	2	4	9	32	20
1	11	0	32	27	0	4	5	42	25	1	7	7	37	37	2	6	9	32	39
1	13	0	172	160	0	6	5	37	43	1	9	7	52	60	2	8	9	27	28
1	15	0	162	152	0	8	5	32	12	1	11	7	28	27	3	1	1	27	23
1	17	0	32	29	0	10	5	38	36	1	1	8	162	169	3	3	1	37	30
2	0	0	535	598	0	12	5	35	31	1	3	8	174	157	3	5	1	32	32
2	2	0	250	242	0	2	6	120	132	1	5	8	120	115	3	7	1	32	22
2	4	0	199	192	0	4	6	180	190	2	0	2	230	228	3	9	1	32	24
2	6	0	308	336	0	6	6	142	134	2	0	4	180	169	3	11	1	32	26
2	8	0	362	407	0	8	6	132	148	2	0	6	141	150	3	13	1	27	25
2	10	0	132	113	0	10	6	163	150	2	0	8	192	185	3	15	1	27	12
2	12	0	136	129	0	2	7	32	38	2	2	1	26	17	3	1	2	212	203
2	14	0	282	273	0	4	7	22	12	2	4	1	30	25	3	3	2	164	177
2	16	0	185	192	0	6	7	32	42	2	6	1	48	42					
3	1	0	233	218	0	8	7	26	30	2	8	1	32	16					
3	3	0	25	8	0	10	7	36	47	2	10	1	32	33					
3	5	0	42	46	0	2	8	112	102	2	12	1	30	29					
3	7	0	222	210	0	4	8	118	125	2	14	1	28	30					
3	9	0	98	114	0	6	8	121	114	2	16	1	32	35					
3	11	0	26	29	0	8	8	85	92	2	18	1	35	33					
3	13	0	33	37	0	10	8	93	89	2	2	2	326	333					
3	15	0	35	42	1	1	1	40	46	2	4	2	353	362					
4	0	0	377	371	1	3	1	22	52	2	6	2	189	210					
4	2	0	164	188	1	5	1	36	48	2	8	2	199	198					
4	4	0	131	144	1	7	1	21	30	2	10	2	245	260					
4	6	0	172	165	1	9	1	21	30	2	12	2	211	212					
4	8	0	150	152	1	11	1	25	35	2	14	2	128	135					
4	10	0	97	105	1	13	1	30	27	2	16	2	142	145					
4	12	0	42	45	1	15	1	32	37	2	18	2	152	157					
5	1	0	48	54	1	1	2	406	439	2	2	3	32	23					
5	3	0	40	38	1	3	2	210	231	2	4	3	26	10					
5	5	0	42	40	1	5	2	240	260	2	6	3	30	25					
5	7	0	145	158	1	7	2	303	292	2	8	3	32	32					
0	0	2	267	278	1	9	2	272	262	2	10	3	26	39					
0	0	4	210	213	1	11	2	158	168	2	12	3	26	18					
0	0	6	170	163	1	13	2	232	220	2	14	3	29	22					
0	0	8	226	232	1	15	2	242	231	2	16	3	26	33					
0	0	10	112	110	1	17	2	109	113	2	2	4	163	175					
0	2	1	26	16	1	1	3	60	67	2	4	4	258	250					
0	4	1	42	40	1	3	3	26	33	2	6	4	99	102					
0	6	1	43	55	1	5	3	28	13	2	8	4	92	107					
0	8	1	26	22	1	7	3	36	52	2	10	4	210	200					
0	10	1	50	42	1	9	3	26	23	2	12	4	132	143					
0	12	1	26	23	1	11	3	26	15	2	14	4	145	140					
0	14	1	53	50	1	13	3	26	24	2	16	4	113	120					
0	16	1	22	10	1	15	3	21	26	2	18	4	152	158					
0	18	1	33	32	1	17	3	27	29	2	2	5	25	27					
0	2	2	183	178	1	1	4	129	137	2	4	5	32	14					
0	4	2	262	253	1	3	4	454	428	2	6	5	32	41					
0	6	2	253	244	1	5	4	266	289	2	8	5	27	32					
0	8	2	231	226	1	7	4	79	83	2	10	5	27	27					
0	10	2	290	278	1	9	4	158	172	2	12	5	32	35					
0	12	2	163	158	1	11	4	334	334	2	14	5	35	36					
0	14	2	212	203	1	13	4	210	215	2	16	5	32	30					
0	16	2	115	110	1	15	4	204	210	2	2	6	57	48					
0	18	2	86	83	1	1	5	23	13	2	4	6	128	118					

Table 4. *Interatomic distances and angles*

Hg^I–$Br(1)^I$	2·67 Å	$Br(1)^I$—Hg^I–$Br(2)^{II}$	111°
Hg^I–$Br(2)^I$	2·51	$Br(3)^{IV}$–Hg^I–$Br(3)^{IV}$	109
Hg^I–$Br(3)^{IV}$	2·41 (twice)	$Br(1)^I$—Hg^I–$Br(3)^{IV}$	104
O^I—$Br(1)^I$	2·91	$Br(2)^I$—Hg^I–$Br(3)^{IV}$	101
O^I—$Br(2)^{III}$	2·77 (twice)		
K^I—O^I	3·45		
K^I—O^{IV}	3·02 (twice)		
K^I—$Br(1)^I$	3·03		
K^I—$Br(2)^{II}$	3·46		

(The standard deviation for the bond lengths is 0·010 to 0·016 Å and for the angles 1·8°.)

Roman numerals indicate the positions of the atoms:

I	0	y	z
II	0	$\bar{y}$	$\frac{1}{2}+z$
III	$\frac{1}{2}$	$\frac{1}{2}+y$	z
IV	$\frac{1}{2}$	$\frac{1}{2}-y$	$\frac{1}{2}+z$

The electronic structure of the water molecule consists of two O–H orbitals and two lone-pair orbitals directed approximately tetrahedrally away from the oxygen atom. In hydrates, where hydrogen bond acceptor groups are available, the O–H orbitals are generally used in the formation of hydrogen bonds. But the lone pair coordination can be of several types. In $KHgBr_3H_2O$ it appears that each of the two lone pairs are directed towards the monovalent metal ion potassium, as in $LiK_2P_3O_9H_2O$ (Eanes & Ondik, 1962) and KF. $2H_2O$ (Anderson & Lingafelter, 1951). The potassium ion has three oxygen atoms and two bromine atoms distributed in an irregular fashion around it at distances ranging from 3·02 to 3·46 Å. These distances are in agreement with the available data on K–Br and K–O coordination. (*International Tables for X-ray crystallography*, 1962).

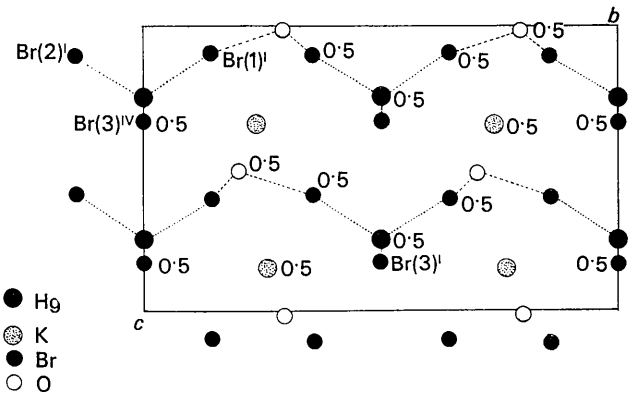

Fig. 1. Projection of the structure along the *a* axis. The dotted line shows Hg–Br coordination and the broken line indicates hydrogen bonding. The number near the atom represents the height of the atom above the plane.

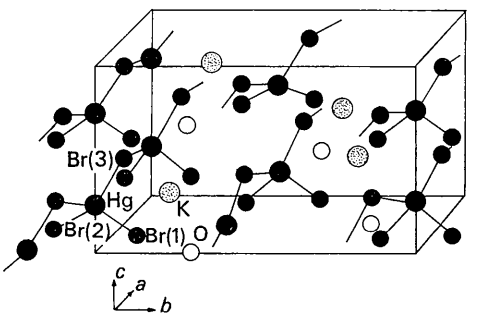

Fig. 2. A perspective view of the unit cell of $KHgBr_3.H_2O$.

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