

The Crystal Structure of CsI₂Br

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The structure of CsI₂Br has been determined by X-ray diffraction. The unit cell is orthorhombic, space group *Pmcn*, with dimensions $a=6.634$ (0.008), $b=9.567$ (0.012), and $c=10.958$ (0.008) Å, where the quantities in parentheses are standard deviations. The cell contains 4 formula units and all atoms lie on mirror planes. The structure was refined by three-dimensional least squares to $R=0.056$. The anion dimensions are Br-I(2)=2.906 and I(2)-I(3)=2.777 Å, and Br-I(2)-I(3)=178.0°. The compound is isostructural with CsI₃.

Introduction

The structure of CsI₂Br has been studied for comparison with that of CsI₃ (Tasman & Boswijk, 1955, hereafter referred to as TB; Mooney, 1935) and to verify that the anion is (I-I-Br)⁻ as expected. Cesium triiodide is one of the unsymmetrical triiodides; structural data for related compounds should help to interpret the forces acting to distort the ion and the bonding in the ion. A comprehensive review of the structures of polyhalides has been presented by Wiebenga, Havinga & Boswijk (1961).

Early optical study of CsI₂Br and CsI₃, as well as other polyhalides, by Wells & Penfield (1892; hereafter referred to as WP) indicated them to be orthorhombic and isostructural.

Description and discussion of the structure

X-ray diffraction data show that CsI₂Br is isostructural with CsI₃, the structure of which was determined by Mooney (1935) and refined by TB. Crystal data and atomic parameters are set out in subsequent sections. The structure is illustrated in Fig. 1, and important interatomic distances are given in Table 1.

Table 1. *Interatomic distances in CsI₂Br*

All distances are in Å and are not corrected for the effects of thermal motion. The non-bonded distances are those indicated by dashed lines in Fig. 1. They are listed clockwise, starting at the top, around each atom, except that repetitions are omitted.

Br-I(2)	2.906	I(2)-I(3)	2.777
Cs...I(3)	4.050 (2×)	Cs...Br	3.581
Cs...Br	3.672	I(2)...I(3)	4.311 (2×)
Cs...I(3)	3.993	I(2)...I(2)	4.407 (2×)
Cs...Br	3.748 (2×)	I(2)...I(3)	3.923
Cs...I(3)	3.948	Br...I(3)	3.965
Cs...I(2)	4.041 (2×)		

The standard deviation in an interatomic distance amounts to about 0.2% of the distance, when the contributions from axial length errors are included.

The most prominent feature is the triatomic anion I₂Br⁻. Comparison of the bond lengths in CsI₂Br,

$$\text{Br}^{2.906}\text{I}(2)^{2.777}\text{I}(3),$$

with those in CsI₃,

$$\text{I}(1)^{3.04}\text{I}(2)^{2.83}\text{I}(3),$$

shows two features. (1) The I(2)-I(3) bond is shorter in I₂Br⁻, and thus closer to the bond length 2.68 Å in crystalline I₂ (Kitaigorodskii, Khotsyanova & Struchkov, 1953) or the length 2.66 Å in the vapor (Karle, 1955). (2) The Br-I(2) bond is longer than would be expected merely from the I(1)-I(2) bond length and the fact that the covalent radius of bromine is about 0.20 Å less than that of iodine. These features suggest that the I₂Br⁻ structure is closer to the situation described as Br⁻ plus I₂ than is the I₃⁻ structure to I⁻ plus I₂. This is just what would be expected from the greater electronegativity of bromine relative to iodine. The bromine atom is bonded, nevertheless, to I(2) because their separation is far less than the sum of van der Waals

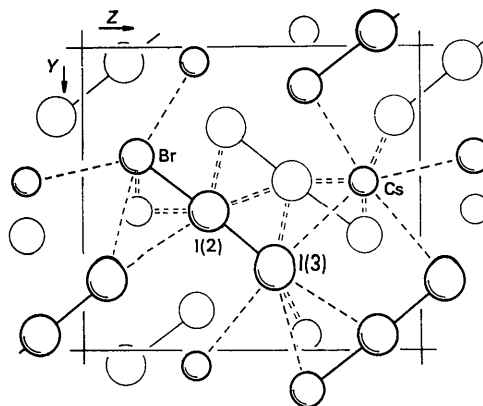


Fig. 1. The structure of CsI₂Br projected onto the *bc* plane. The heavily outlined atoms lie at $x=\frac{1}{4}$, the lightly outlined ones at $x=-\frac{1}{4}$ or $\frac{3}{4}$. *c*-Glide planes are located at $y=\frac{1}{4}$ and $\frac{3}{4}$, *n*-glide planes at $z=\frac{1}{4}$ and $\frac{3}{4}$. The dashed lines are non-bonded distances; a double dashed line indicates two distances, to atoms above and below the plane at the heavily outlined atoms.

radii, 4.1 Å. This polarization of I_2Br^- inferred from bond lengths receives some support from the fact that the bromine atom occupies a site of higher electrostatic potential than does iodine atom I(3); the sum of $1/r$ values for the four nearest cesium ions in each case amount to 1.085 at Br, 0.999 at I(3). (The corresponding values in CsI_3 are 1.046 and 0.971). Some feeling for the significance of this difference may be gained by noting that if half an electron, for example, is moved from I(3) to Br, the electrostatic energy is reduced by 14 kcal.mole⁻¹.

The bond angle Br-I(2)-I(3) is 178.0°, deviating from linearity in the direction which displaces I(2) toward the center of the unit cell. The corresponding angle is 176.3° in CsI_3 .

Table 1 includes all non-bonded distances less than 4.5 Å. The values must be compared with the corresponding sum of ionic or van der Waals radii, namely, 3.64 Å for Cs ··· Br, 3.84 for Cs ··· I, 4.10 for Br ··· I, and 4.30 for I ··· I. The only distances shorter than the expected van der Waals distances are Cs ··· Br = 3.581, Br ··· I(3) = 3.965, and I(2) ··· I(3) = 3.923 Å. The last of these is the most striking, being almost 0.4 Å shorter than the normal van der Waals distance. This, plus the fact that atom I(2) is not far from collinear with the ion to which I(3) belongs, suggests a description of the bonding in the group Br-I(2)-I(3) ··· I(2) as 4-center, 6-electron bonding (Rundle, 1963). Short 'nonbonded' I ··· I distances are, of course, common. One of the more extreme examples is provided by iodine monochloride in both α (Boswijk, van der Heide, Vos & Wiebenga, 1956) and β forms (Carpenter & Richards, 1962) where the shortest I ··· I distances are 3.08 and 3.06 Å, respectively.

All interatomic distances quoted previously are uncorrected for the effects of thermal motion. Application of Cruickshank's (1956) analysis of the atomic displacements into rigid-body motions seems to be inappropriate for the anion because the atom (bromine) farthest from the center of mass of the ion does not exhibit the largest amplitudes (*cf.* Table 2). Application of the Busing & Levy (1964) analysis is straightforward, but there is no adequate basis here for knowing what kind of correlation is present between the thermal displacements of bonded atoms. For Br-I(2), the latter analysis gives 2.907 Å as lower bound, 2.942 as upper bound and

2.924 for uncorrelated motion. Similarly for I(2)-I(3) the values are 2.778, 2.818, and 2.798 Å respectively. In the absence of more information, the values for uncorrelated motion of the atoms probably represent the best estimates of bond distances here.

Experimental

Sample preparation

Crystals of CsI_2Br were prepared according to the method of WP by adding iodine to cesium bromide dissolved in a mixture of alcohol and water. In view of difficulties experienced previously in attempting to prepare $N(CH_3)_4I_4Br$, care was taken to verify that the product was the desired one and not CsI_3 . Analysis showed I, 51.1 (calc. 54.39)%, Br, 17.2 (calc. 17.13)%, and preliminary photographs prepared from several medium-sized crystals exhibited distinct differences from photographs of CsI_3 .

Unit cell

Preliminary rotation and Weissenberg photographs showed that CsI_2Br is orthorhombic and isostructural with CsI_3 , and provided approximate cell dimensions. This confirms the conclusions of WP. The axes are labelled to correspond to those used for CsI_3 by TB.

A powder sample, to which silicon powder had been added for calibration purposes, was examined with copper radiation in a Philips diffractometer. On the basis of the approximate cell dimensions, ten powder lines in the range $\theta < 17^\circ$ could be indexed unambiguously as individual reflections, and two silicon lines appeared in the useful region. The axial lengths were then adjusted by the method of least squares to reproduce as well as possible the measured values of $(\sin \theta)^2$. The results are

$$a = 6.634, \quad b = 9.567, \quad c = 10.958 \text{ \AA}$$

with standard deviations respectively 0.008, 0.012, and 0.008 Å. Since the indexed lines are at rather small angles, the systematic errors may be as large as the random errors which these figures indicate. Consequently it is estimated that more realistic measures of accuracy are estimated standard deviations double those from least squares, namely 0.016, 0.024, and 0.016 Å in a , b , and c respectively. The calculated axial ratios 0.6934 : 1 : 1.1454 agree satisfactorily with values 0.6916 : 1 : 1.1419 determined by optical goniometry (WP).

The density of CsI_2Br may be roughly estimated as 4.4 g.cm⁻³ by interpolation between the pycnometric values for CsI_3 and $CsIBr_2$ reported by Bozorth & Pauling (1925). The X-ray value, on the assumption of 4 formula units per cell, is 4.456 g.cm⁻³, thus confirming the assumption.

Space group

The systematic absences $h0l$ for l odd and $hk0$ for $h+k$ odd imply either space group $P2_1cn$ or $Pm\bar{c}n$ ($Pnma$ relabelled). The crystal morphology (WP) seems

Table 2. Final parameters for CsI_2Br

All atoms lie on the mirror plane at $x = \frac{1}{4}$, and $U_{12} = U_{31} = 0$. All values have been multiplied by 10^4 . Coordinates are in fractions of cell edges and vibration tensor components in Å². Beneath each value is the corresponding standard deviation.

Atom	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$
Cs	4506	8357	337	498	390	-117
	3.3	2.6	46	17	13	26
Br	3670	1628	263	328	286	-99
	4.6	3.7	68	20	18	32
I(2)	5495	3749	128	338	325	86
	2.9	2.4	46	12	12	22
I(3)	7318	5721	306	335	421	-138
	3.1	2.7	47	13	15	23

to be centrosymmetric, so *Pm*cn was assumed here, as for CsI₃ (TB). The subsequent refinement verifies this choice.

Structure factor magnitudes

All intensities were measured with a single small well-formed crystal having dimensions 0.15 × 0.08 × 0.12 mm along *a*, *b*, and *c*, respectively. It was mounted to rotate about *c*.

Intensities were measured on multiple-film integrated equi-inclination Weissenberg photographs by means of a Nonius microdensitometer. Weak spots were measured by visual comparison of spots on strongly exposed non-integrated photographs with a set of standard spots. Ilford film types Industrial G, B, and C were placed one behind the other in the film holder and exposed simultaneously with zirconium-filtered Mo *K*α radiation. The layers *h* = 0, 1, 2, and 3 were measured, as well as a special integrated Weissenberg photograph containing a 35° sample from each layer. This last record enabled the intensity values from the four layers to be placed on the same scale. It also showed that some deterioration of the crystal had occurred during the exposures; the strong spots had become relatively more intense than on earlier films because of reduced extinction. For this reason, as well as because the *x* coordinates of the structure were known from symmetry grounds, higher *h* levels were not measured.

The intensities were corrected approximately for absorption by means of a computer program devised for two-dimensional corrections for zero-layer data from crystals with uniform cross-section perpendicular to the rotation axis. It was applied to upper layers by using an increased absorption coefficient to simulate the effect of increased path length. An inadvertent blunder provided an interesting measure of success of this absorption correction. Initially the orientation of the crystal was introduced 90° away from its correct orientation about the rotation axis so that the longer and shorter crystal dimensions in the cross section were interchanged. When this error was corrected during the refinement, the usual discrepancy index *R* (for observed reflections only) dropped immediately from 16% to 10%.

Structure factor magnitudes were then extracted from the corrected intensities in the usual way. Finally the various values from symmetrically equivalent reflections were averaged; in most cases, two or three values contributed to the average. A total of 367 independent reflections were measured.

The refinement

Since CsI₂Br is isostructural with CsI₃, the atomic coordinates of the latter (TB) were used as a first approximation. All atoms are in special positions 4(*c*), the mirror planes at *x* = $\frac{1}{4}$ and $\frac{3}{4}$.

Initial refinement was carried out with *h* = 0 data. First the electron density projection was calculated with signs from CsI₃ for all but the smaller structure factors. The result appeared generally reasonable and the peak corresponding to I(1) in CsI₃ was significantly lower than the others and so probably bromine. This atom was identified as bromine for a structure factor calculation, and another Fourier synthesis was evaluated with inclusion of all observed structure factors. The refined parameters gave *R* = 24% at this stage. Thereafter numerous cycles of isotropic least squares refinement led to nearly complete convergence at *R* = 8.6%. Extra cycles were needed as a result of correcting the absorption corrections (described in the *Experimental* part) and to verify that the proper atom had been identified as bromine. A parallel refinement with all halogen atoms identified as iodine converged to *R* = 13.2%, a convincingly poorer result.

At this point data from higher layers were included and least-squares refinement was resumed on the XI computer at Leiden with the block-diagonal least-squares program of Drs E. Rutten-Keulemans. Convergence was achieved in seven cycles of refinement, including anisotropic temperature factor parameters. A fraction 0.8 of calculated coordinate shifts, 0.6 of calculated temperature parameter shifts, were applied. Subsequently it was apparent that use of full shifts would have accelerated the convergence, so full shifts were applied at the last cycle to obtain the final parameters. The largest coordinate change from the result of the *h* = 0 refinement was 0.01 Å, and the average change was 0.005 Å. The coordinates differ from those of CsI₃ by an average of only 0.05 Å, but the maximum change, for *y*(Cs) × *b*, amounts to 0.13 Å.

The final parameters of the structure are given in Table 2. For all atoms *x* = $\frac{1}{4}$ and *U*₁₂ = *U*₃₁ = 0 by symmetry. The standard deviations are those calculated by the least-squares procedure using the diagonal approximation. The labelling of the atoms corresponds to that in Fig. 1 and is like that used for CsI₃.

The observed and calculated structure factors are set out in Table 3. A few corrections of then-obvious errors in the observed values have been made since the last cycle of least squares, chiefly rejection of those reflections too weak to be seen on re-examination of the films; the corrected values are marked. Unobserved reflections were not carried through the refinement, on grounds of efficiency. At the end, threshold values were estimated for 150 unobserved reflections by consideration of minimum observed values in neighboring regions of reciprocal space and of the presence of nearby observed reflections to serve as landmarks. For 21 of the 150 unobserved reflections, the calculated structure factor magnitude is larger than the observed, but never as much as 40% larger. The final value of the conventional discrepancy index, for unweighted observed reflections only, was *R* = 5.6%.

A final difference synthesis, based on the structure factors in Table 3, showed no peaks higher than 1.71

Table 3. Observed and calculated structure factors for CsI₂Br

The values listed are $5F_o$ and $5F_c$. The maximum value for a reflection too weak to observe is given a negative value under F_o . A dash in the F_o column means that the reflection was obscured by the beam stop. Corrected F_o values (see text) are indicated by asterisks.

K	L	F _O	F _C	K	L	F _O	F _C	K	L	F _O	F _C	K	L	F _O	F _C	K	L	F _O	F _C
H = 0																			
				8	7	-100	68	1	3	512	463	4	12	-115	63	0	8	176	160
				9	7	238	-263	2	3	1250	-1272	5	12	166	-157	1	8	277	254
2	0	607	574	10	7	-120	79	3	3	539	505	6	12	-120	-64	2	8	525	-552
4	0	674	669	11	7	135	139	4	3	1014	-993	7	12	240	-222	3	8	268	-278
6	0	641	-631	0	8	191	-192	5	3	316	-310	1	13	205	-197	4	8	129	133
8	0	107	-95	1	8	273	-278	6	3	426	-417	2	13	-120	124	5	8	344	-341
10	0	621	-651	2	8	592	595	7	3	176	153	3	13	238	-239	6	8	-115	-115
12	0	246	-287	3	8	289	308	8	3	447	-479	7	8			7	8	287	-264
1	1	--	35	4	8	154	-151	9	3	410	-417	H = 2				8	8	289	294
2	1	252	-240	5	8	359	373	10	3	-110	-106	2	0	584	-502	9	8	-120	113
3	1	115	73	6	8	102	85	11	3	-120	46	4	0	576	-594	1	9	703	-729
4	1	1254	-1308	7	8	279	288	0	4	949	-977	4	0	576	-594	2	9	234	196
5	1	412	424	8	8	328	-312	1	4	-110	-62	6	0	568	571	3	9	205	-185
6	1	902	-921	9	8	125	-119	2	4	135	118	8	0	135	93	4	9	156	141
7	1	512	-503	1	9	781	791	3	4	59	57	10	0	580	606	5	9	195	159
8	1	371	-395	2	9	215	-210	4	4	1008	-1008	12	0	234	269	6	9	350	372
9	1	225	117	3	9	205	200	5	4	564	-518	1	1	-100	-50	7	9	-115	-33
10	1	227	217	4	9	174	-147	6	4	500	498	2	1	229	214	8	9	-115	-29
11	1	168	-181	5	9	174	-173	7	4	223	-210	3	1	107	-73	9	9	281	254
12	1	-120	-30	6	9	379	-398	8	4	-115	156	4	1	1104	1165	0	10	371	390
0	2	--	-175	7	9	-105*	30	9	4	-115	14	5	1	375	-379	1	10	340	311
1	2	305	299	8	9	-110	25	10	4	174	170	6	1	814	840	2	10	131	86
2	2	893	-854	9	9	229	-272	11	4	-120	63	7	1	473	464	3	10	90	89
3	2	994	-931	0	10	389	-426	1	5	234	-203	8	1	359	364	4	10	-115	-40
4	2	508	474	1	10	371	-338	2	5	-100	-25	9	1	-110	-108	5	10	652	698
5	2	611	609	2	10	78	-94	3	5	504	474	10	1	229	-200	6	10	-115	-31
6	2	260	-267	3	10	-100	-83	4	5	-100	-25	11	1	203	171	7	10	191	189
7	2	232	-211	4	10	-100	42	5	5	-105	-45	0	2	119	144	1	11	271	286
8	2	174	157	5	10	707	-750	6	5	428	-406	1	2	250	-244	2	11	215	200
9	2	115	-89	6	10	-105	33	7	5	-110	-21	2	2	752	730	3	11	189	165
10	2	-100*	61	7	10	205	-200	8	5	184	170	3	2	836	832	4	11	-120	-152
11	2	-110	-56	1	11	289	-306	9	5	215	-217	4	2	439	-421	5	11	-120	-43
12	2	-120	103	2	11	232	-212	10	5	-115	-77	5	2	525	-526	6	12	260	-235
1	3	715	657	3	11	180	-176	11	5	258	242	6	2	242	242	1	12	143	122
2	3	186	-150	4	11	129	138	0	6	844	-850	7	2	227	203	2	12	182	155
3	3	359	-303	5	11	-105	44	1	6	949	-992	8	2	174	-142	3	12	-115	-127
4	3	799	-767	6	11	-110	38	2	6	320	-280	9	2	-110	75	4	12	-120	43
5	3	160	-151	0	12	260	263	3	6	221	-198	10	2	-120	-57	5	12	-130	155
6	3	-100*	-76	1	12	107	-133	4	6	404	-384	1	3	598	-545	1	13	299	275
7	3	188	159	2	12	129	-160	5	6	461	-467	2	3	166	140	2	13	-115	-80
8	3	402	-426	3	12	113	122	6	6	285	280	3	3	307	278	3	13	-120	101
9	3	-100	100	4	12	-110	-49	7	6	-110	66	4	3	701	695	4	13	-130	-16
10	3	227	246	5	12	-120	-156	8	6	227	198	5	3	182	138	5	13	-130	-100
11	3	-120	-162	1	13	271	-294	9	6	260	-289	6	3	82	70	0	14	-115	-61
12	3	-130	-92	2	13	-110	87	10	6	256	270	7	3	191	-152	1	14	-115	-9
0	4	1563	-1736	3	13	115	-100	1	7	570	-568	8	3	373	394	2	14	-120	147
1	4	869	844	4	13	-120	-9	2	7	488	493	9	3	-110	-96	3	14	-130	-142
2	4	772	-747	5	13	-130	101	3	7	621	-649	10	3	227	-227	4	14	-130	-103
3	4	861	-860	0	14	-110	60	4	7	650	680	0	4	1389	1535	5	14	313	-283
4	4	201	-176	1	14	-115	13	5	7	-110	-111	1	4	729	-739	1	15	260	-243
5	4	262	-242	2	14	-120	-147	6	7	-110	58	2	4	662	674	2	15	-120	-79
6	4	252	249	3	14	-130	153	7	7	361	356	3	4	750	761	H = 3			
7	4	580	-596	4	14	-150	103	8	7	371	404	4	4	189	161	1	0	352	-367
8	4	258	251	5	14	275	301	9	7	313	318	5	4	229	218	3	0	846	795
9	4	242	236	1	15	252	260	0	8	314	319	6	4	254	-229	5	0	746	-772
10	4	375	365	2	15	-130	84	1	8	-110	-106	7	4	518	542	7	0	-110	98
11	4	-120	-4					2	8	186	172	8	4	250	-237	9	0	-110	2
12	4	186	225					3	8	822	814	9	4	254	-218	7	0	-110	98
1	5	953	-935					4	8	471	490	10	4	344	-343	9	0	-110	2
2	5	326	328	1	0	--	485	5	8	139	154	1	5	820	841	11	0	-130	104
3	5	207	-146	3	0	1012	-1081	6	8	209	-193	2	5	303	-296	1	1	164	-145
4	5	752	735	5	0	920	908	7	8	410	461	3	5	162	136	2	1	869	-860
5	5	152	-150	7	0	164	-147	8	8	211	-227	4	5	664	-670	3	1	262	221
6	5	1049	1083	9	0	-100	-8	1	9	303	303	5	5	141	135	4	1	424	-416
7	5	322	313	11	0	-120	-117	2	9	322	-327	6	5	930	-994	5	1	277	265
8	5	154	39	1	1	--	154	3	9	-110	-7	7	5	287	-290	6	1	598	-610
9	5	-100	97	2	1	1109	1122	4	9	-110	56	8	5	-110	-14	7	1	305	-313
10	5	-110	43	3	1	359	-311	5	9	154	139	9	5	-110	-90	8	1	-110	-44
11	5	307	326	4	1	525	498	6	9	-115	42	10	5	-115*	-41	9	1	-120	73
12	5	186	-153	5	1	355	-327	7	9	193	-157	11	5	305	-305	10	1	271	-246
0	6	522	497	6	1	721	729	0	10	543	547	0	6	453	-445	11	1	-120	52
1	6	467	446	7	1	383	388	1	10	145	132	1	6	424	-405	12	1	207	237
2	6	906	943	8	1	-100	43	2	10	211	-218	2	6	799	-843	0	2	422	-419
3	6	266	223	9	1	-100	-72	3	10	277	302	3	6	244	-214	1	2	672	-660
4	6	465	-534	10	1	281	289	4	10	-110	108	4	6	486	485	2	2	1545	-1553
5	6	566	549	11	1	-105	-50	5	10	-115	-3	5	6	498	-512	3	2	-110*	16
6	6	268	258	12	1	273	-273	6	10	125	-144	6	6	262	-237	4	2	289	-268
7	6	146	129	0	2	--	506	7	10	-120	66	7	6	-110	-142	5	2	359	-343
8	6	133	-140	1	2	900	884	1	11	340	316	8	6	100	126	6	2	-115	44
9	6	186	188	2	2	1719	1996	2	11	-110	2	9	6	-120	-141	7	2	-115	84
10	6	-120	-136	3	2	-100	-17	3	11	299	300	1	7	14					

and no holes deeper than $-2.51 \text{ e.}\text{\AA}^{-3}$; these extreme values are found near iodine atoms. The estimated standard deviation in the density amounts to about $0.66 \text{ e.}\text{\AA}^{-3}$ according to the formula of Cruickshank & Rollett (1953). All atomic centers lie on nearly flat regions.

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The Crystal Structure of Rh₂Te₃

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The compound Rh₃Te₂ is orthorhombic, space group *Amam*, with four molecules in the cell, $a = 7.694$, $b = 12.446$, $c = 3.697 \text{ \AA}$.

The structure is of a new type. There are two kinds of rhodium and two kinds of tellurium atom in the structure. The number and mean lengths of the bonds are: Rh_I-5Te = 2.69 Å, Rh_I-4Rh = 2.84 Å, Rh_{II}-5Te = 2.68 Å, Rh_{II}-5Rh = 2.94 Å, Te_I-8Rh = 2.73 Å, Te_{II}-7Rh = 2.66 Å.

Introduction

During a recent visit to the Physics Department of the University of California at San Diego the writer examined X-ray diffraction patterns of numerous preparations in the Rh-Te system. It was shown by indexing of the powder pattern that samples obtained by quenching from the melt at the exact composition Rh₃Te₂ contained a single phase. Small departures from the ideal stoichiometric ratio resulted in two-phase preparations, the second phase being Rh metal on the Rh-rich side and the high-temperature form (NiAs type) of RhTe (Geller, 1954) on the Te-rich side.

Variations in the lattice spacings of Rh₃Te₂ were not observed. It must be concluded that the homogeneity range is very narrow and that the structure is fully ordered.

Upon annealing for days at 450°C Rh₃Te₂ is transformed into rhodium metal and a new phase of approximate composition Rh:Te ≈ 1.1. However, this new phase is not identical with the low temperature form of RhTe.

References

- BOSWIJK, K. H., VAN DER HEIDE, J., VOS, A. & WIEBENGA, E. H. (1956). *Acta Cryst.* **9**, 274.
 BOZORTH, R. M. & PAULING, L. (1925). *J. Amer. Chem. Soc.* **47**, 1561.
 BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
 CARPENTER, G. B. & RICHARDS, S. M. (1962). *Acta Cryst.* **15**, 360.
 CRUICKSHANK, D. W. J. & ROLLETT, J. S. (1953). *Acta Cryst.* **6**, 705.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
 KARLE, I. L. (1955). *J. Chem. Phys.* **23**, 1739.
 KITAIGORODSKII, A. I., KHOTSYANOVA, T. L. & STRUCHKOV, Y. T. (1953). *Zh. Fiz. Khim.* **27**, 780.
 MOONEY, R. C. L. (1935). *Z. Kristallogr.* **90**, 143.
 RUNDLE, R. E. (1963). *J. Amer. Chem. Soc.* **85**, 112.
 TASMAN, H. A. & BOSWIJK, K. H. (1955). *Acta Cryst.* **8**, 59.
 WELLS, H. L. & PENFIELD, S. L. (1892). *Z. anorg. Chem.* **1**, 85.
 WIEBENGA, E. H., HAVINGA, E. E. & BOSWIJK, K. H. (1961). *Advanc. Inorg. Chem.* **3**, 133.

The structure

The analysis of the powder patterns of Rh₃Te₂ gave an orthorhombic base centered translation lattice *A* with periods.

$$a = 7.694 \pm 0.004, b = 12.446 \pm 0.008, c = 3.697 \pm 0.002 \text{ \AA}.$$

The calculated density with four molecules per cell is $\rho = 10.56 \text{ g.cm}^{-3}$.

The approximate structure was readily deduced from the powder data with the following results:

Space group: *Amam*

4Me in 4(*a*): (000) ($\frac{1}{2}$ 00)

4Me in 4(*c*₁): $\pm (\frac{1}{2}y_1 0)$ with $y_1 \approx 0.53$

4Me in 4(*c*₂): $\pm (\frac{1}{2}y_2 0)$ with $y_2 \approx 0.745$

8Me in 8(*f*): $\pm (x_3 y_3 0) (\frac{1}{2} + x_3, \bar{y}_3, 0)$

with $x_3 \approx 0.06$ $y_3 \approx 0.34$.

However, it was not possible to distinguish between Rh and Te atoms.

Subsequently one single crystal was isolated from one of the quenched samples. The crystal was 2 mm