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The Crystal Structure of Caesium Bismuth Iodide, $Cs_3Bi_2I_9$

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The crystal structure of caesium bismuth iodide, $Cs_3Bi_2I_9$, has been determined. The crystals are of hexagonal symmetry with $a = 8.411_6$ Å and $c = 21.18_2$ Å, and belong to the space group $P6_3/mmc$.
The structure was solved by means of three-dimensional electron density calculations and refined by least squares methods, using 454 independent reflections, a final R value of 0.105 being obtained.
The dominating component of the structure is the $Bi_2I_9^{3-}$ ion, which appears as two iodine octahedra sharing a face, each octahedron having a bismuth atom at its centre. The $Bi-I_{bridge}$ and $Bi-I_{terminal}$ bond distances are 3.249 Å and 2.923 Å, respectively, the standard deviation being 0.005 Å. The three-dimensional arrangement in the structure is best described as a close packing of the caesium and iodine atoms. The average Cs–I distance is 4.24 Å.

The crystal structure of caesium bismuth iodide, $Cs_3Bi_2I_9$, was investigated to determine the Bi–I configuration in the solid state. It was also considered interesting to see how the packing of the caesium and iodine ions is influenced by the presence of the bismuth(III) ions. This work was undertaken in connection with solubility studies [1] of Bi_2O_3–BiOI in 1 M and 3 M $(H,Na)(ClO_4,I)$ as a function of $[H^+]$ and $[I^-]$.

EXPERIMENTAL

Crystals of caesium bismuth iodide were prepared by allowing an aqueous solution of caesium nitrate to diffuse into a solution of sodium iodide and bismuth(III) oxide in acetic acid.[2] The two solutions were stratified in a glass tube inclined at 45° to the horizontal plane and arranged so as to make possible the removal of crystals during growth without destroying the diffusion zone. The crystals, which formed on the walls of the glass tube, were red-brown hexagonal bipyramids.

Analysis of the material gave a ratio of $Bi:Cs:I = 1:1.4_1:4.6_7$, which suggests the formula $Cs_3Bi_2I_9$. The *bismuth* content was determined spectrophotometrically, the *caesium* content by atomic absorption spectrophotometry, and the *iodine* content by titration with a standard solution of silver nitrate.

Table 1. Guinier powder data for $Cs_3Bi_2I_9$. $\lambda(CuK\alpha_1) = 1.54050$ Å. The multiplicity factor factor is not included in F_{calc}.

h k l	$10^5 \cdot \sin^2\theta$ obs	$10^5 \cdot \sin^2\theta$ calc	*I* obs	$F \times 10^{-1}$ calc
0 0 2	529	529	w	
0 1 0	1117	1118	s	16
0 1 1	1247	1250	vvs	21
0 1 2	1644	1647	w	10
0 0 4	2108	2116	m	31
0 1 3	2303	2308	w	8
0 1 4	3235	3234	w	14
1 1 0	3351	3354	s	26
1 1 2	3883	3883	m	11
0 1 5	4417	4424	s	25
0 2 0	4472	4472	w	16
0 2 1	4602	4604	w	11
0 0 6	4750	4760	vs	77
0 2 2	4995	5001	vvs	43
1 1 4	5457	5470	s	24
0 2 3	5652	5662	vvs	44
0 1 6	5880	5878	m	15
0 2 4	6582	6588	vvs	46
0 1 7	7603	7597	w	16
0 2 5	7770	7778	vs	46
1 2 0	7820	7826	m	16
1 2 1	7952	7958	vs	20
1 1 6	8112	8114	m	25
1 2 2	8335	8355	vw	5
0 2 6	9231	9232	w	13
1 2 4	9943	9942	w	11
0 3 0	10063	10062	m	30
0 3 2	10596	10591	vw	11
0 2 7	10949	10951	m	29
1 2 5	11130	11132	m	19
0 1 9	11820	11828	vw	18
0 3 4	12174	12178	w	19
1 2 6	12565	12586	vw	10
0 2 8	12937	12934	s	38
0 0 10	13211	13222	vw	33
2 2 0	13411	13416	vvs	79
2 2 2	13932	13945	vw	8
0 1 10	14324	14340	w	18
1 3 0	14540	14534	vw	12
1 3 1	14672	14666	m	15
3 0 6	14814	14822	vw	19
0 2 9	15190	15182	vs	47
2 2 4	15533	15532	vw	13
1 3 3	15724	15724	vw	7
1 1 10	16557	16576	w	19
0 1 11	17115	17117	w	23
0 2 10	17680	17694	w	19
1 3 5	17837	17840	m	18
2 2 6	18174	18176	s	42
0 4 2	18406	18417	s	31
0 0 12	19046	19040	s	61
1 3 6	19297	19294	vw	9

Table 1. Continued.

0 4 4	19994	20004	s	32
1 3 7	21010	21013	vw	10
0 4 5	21204	21194	m	30
2 3 1	21368	21374	vw	10
1 1 12	22403	22394	vw	14
0 4 6	22612	22648	vw	11
0 3 10	23286	23284	vw	17
1 4 0	23471	23478	m	20
0 4 7	24368	24367	vw	21
2 3 5	24535	24548	w	20
1 3 9	25250	25244	vw	9
1 4 4	25577	25594	w	14
2 3 6	25998	26002	vw	11
0 4 8	26345	26350	w	26
2 2 10	26616	26638	vw	21
2 3 7	27696	27721	w	14
0 5 1	28083	28082	w	18
1 4 6	28258	28238	w	15
0 4 9	28585	28598	m	30
0 2 14	30366	30387	w	34
1 3 11	30539	30533	vw	13
0 1 15	30839	30868	vw	16
0 5 5	31250	31256	vw	11
2 4 2	31838	31833	m	23
2 2 12	32463	32456	s	46
2 4 4	33405	33420	m	27
2 4 5	34591	34610	m	26
1 4 10	36707	36700	vw	12
2 4 7	37797	37783	vw	15
1 5 6	39387	39418	vw	6
2 4 8	39730	39766	w	24
0 6 0	40251	40248	s	45
3 4 1	41519	41498	vw	15
2 4 9	42013	42014	w	25
0 6 5	43530	43553	vw	5
0 4 14	43841	43803	vw	22
0 6 6	44985	45008	vw	18
2 5 4	45739	45718	vw	10

SPACE GROUP AND UNIT CELL

Weissenberg films $0kl-5kl$ and $hk0$ and the corresponding rotation photographs were recorded. The crystals, which are of hexagonal symmetry with the Laue group $6/mmm$, gave no systematic absences other than hhl absent for $l=2n+1$, suggesting one of the space groups No. 186—$P6_3mc$, No. 190—$P\bar{6}2c$, or No. 194—$P6_3/mmc$.[3]

The cell dimensions of $Cs_3Bi_2I_9$, as determined from the Weissenberg and rotation films, were $a=8.3_8$ Å and $c=21.0_5$ Å. To obtain greater accuracy in these values, Guinier powder films were taken, using KCl as an internal standard ($CuK\alpha_1$ radiation, $\lambda=1.54050$ Å, $a_{KCl}=6.2919_4$ Å at 20°C [4]). Using the computer programme POWDER,[5] 90 reflections were indexed and subsequently refined (*cf.* Table 1), to give the cell dimensions $a=8.4116\pm0.0007$ Å, $c=21.182\pm0.002$ Å, and $V=1298$ Å^3.

Assuming a cell content of two formula units, the calculated density is 5.014 g/cm^3, which seems to be reasonable.[2]

DETERMINATION OF THE STRUCTURE

The $0kl-5kl$ reflections were used for the crystal structure analysis of $Cs_3Bi_2I_9$, the intensities being estimated visually with the aid of an intensity scale which was prepared by timed exposures of a chosen reflection of the actual crystal. Weissenberg multiple film techniques, with six films for each layer line, were used when collecting the data. The film factor was calculated as a mean value of the ratios of the observed intensities for common reflections.

In each layer all reflections within 90° were measured (a total of 775). Thus the reflections khl and hkl with $h\leq5$, $k\leq5$ and $h\neq k$ were estimated twice, those with higher h and k values only once. The number of independent reflections was 454.

Since crystals of $Cs_3Bi_2I_9$ have a linear absorption coefficient of 1450 cm^{-1} for Cu$K\alpha$ radiation, considerable absorption errors in the data had to be corrected for. The crystal used to collect the a axis series was, before mounting, cut perpendicular to the [001] direction, after which it was measured accurately. The main dimensions of the crystal were: 0.12 mm in the [100] and [010] directions and 0.08 mm in the [001] direction. Correction for absorption effects, as well as calculation of Lorenz' and polarization factors were performed using the programme DATAP2.[6] The absorption correction was not made until an approximate structure had been deduced.

A three-dimensional Patterson synthesis was calculated, using all the independent $|F_o|^2$ values. Assuming the space group to be $P6_3/mmc$, the bismuth atoms were found to occupy the position $4(f)$ with $z=0.155$. Before the Patterson function was calculated, approximate scales between the different layer lines were obtained from the corresponding hkl and khl reflections.

Using the signs of the bismuth contributions to the structure factors, a three-dimensional Fourier summation was made, giving the positions of the caesium and iodine atoms:

2	Cs	in	$2(b)$,	
4	Cs	in	$4(f)$	with $z = -0.08$,
6	I	in	$6(h)$	with $x = 0.50$ and
12	I	in	$12(k)$	with $x = 0.16$, $z = 0.08$.

When calculating the Patterson and Fourier maps, the programme DRF[6] was used.

REFINEMENT

All refining work on this structure was done using the least squares, full matrix programme LALS.[6]

A preliminary refinement, reported earlier,[9] using all the 775 F_o values, not yet corrected for absorption effects, gave a rather poor agreement factor of 0.21 ($R=\sum||F_o|-|F_c||/\sum|F_o|$).

After introducing the absorption factors, which varied between 18 and 250, the atomic co-ordinates, isotropic temperature factors and separate scale factors for the different layer lines were refined. After three cycles of refinement of the 775 F_o values the R value dropped to 0.15.

Applying the refined scale factors, the mean value of each corresponding *hkl* and *khl* reflection was calculated, giving 454 independent reflections, on which the final refinement was based. At this stage, anisotropic thermal motions of the atoms were introduced. Since all atoms in this structure are in special positions, there were only 19 parameters to be refined (5 positional co-ordinates, 13 thermal parameters and the overall scale factor), *i.e.* there were 24 observations for each parameter. The atomic scattering factors used were those calculated by Cromer and Waber,[8] and the structure factors were weighted according to Cruickshank:[9] $w=(a+F_o+cF_o^2+dF_o^3)^{-1}$, with $a=70$, $c=0.004$, and $d=0$.

The final R value, obtained after three cycles of refinement, was 0.105. The parameters together with their standard deviations are given in Table 2, and the observed structure factors and those calculated from the parameters of Table 2 are listed in Table 3.

Table 2. Final atomic parameters for $Cs_3Bi_2I_9$ (standard deviations in parentheses). The anisotropic temperature factor is $\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\}$.

		x	y	z
Bi	4(*f*) *	1/3	2/3	0.1544(1)
Cs_1	4(*f*)	1/3	2/3	0.5822(4)
Cs_2	2(*b*)	0	0	1/4
I_1	12(*k*)	0.1637(3)	0.3275(3)	0.0807(2)
I_2	6(*h*)	0.5075(8)	0.0155(8)	1/4

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Bi	0.0118(5)	0.0118(5)	0.0013(1)	0.0118(5)	0	0
Cs_1	0.0254(11)	0.0254(11)	0.0025(2)	0.0254(11)	0	0
Cs_2	0.0207(13)	0.0207(13)	0.0040(3)	0.0207(13)	0	0
I_1	0.0270(9)	0.0169(8)	0.0025(1)	0.0169(8)	−0.0155(8)	−0.0058(8)
I_2	0.0112(6)	0.0344(23)	0.0019(1)	0.0344(23)	0	0

* 2(*b*): $\pm(0,0,1/4)$;
4(*f*): $\pm(1/3,2/3,z)$, $\pm(1/3,2/3,1/2-z)$;
6(*h*): $\pm(x,2x,1/4)$, $\pm(-2x,-x,1/4)$, $\pm(x,-x,1/4)$;
12(*k*): $\pm(x,2x,z)$, $\pm(-2x,-x,z)$, $\pm(x,-x,z)$, $\pm(-x,-2x,1/2+z)$, $\pm(2x,x,1/2+z)$, $\pm(-x,x,1/2+z)$;

Table 3. Calculated and observed structure factors for $Cs_3Bi_2I_9$. (The columns are l, F_o, and F_c, respectively).

l	F_o	F_c
0 0 L		
4	305	-185
6	757	-774
8	67	-30
10	329	-297
12	604	761
14	163	150
16	95	-97
18	326	-306
20	84	74
22	147	-129
24	126	124
26	79	85
0 1 L		
0	165	-142
1	204	193
2	103	57
3	72	66
4	123	103
5	246	-260
6	132	-130
7	166	146
9	169	134
10	163	129
11	204	-178
12	80	-69
14	46	-36
15	147	138
16	64	58
17	90	-91
19	37	-27
20	69	-64
21	96	97
22	64	57
23	38	-27
25	64	-63
26	32	-27
0 2 L		
0	157	-139
1	111	84
2	429	-467
3	449	513
4	464	564
5	474	522
6	125	-120
7	289	-296
8	381	399
9	522	-534
10	244	-200
11	81	-52
12	72	-52
13	110	89
14	330	-308
15	120	108
16	243	242
17	226	223
20	105	93
21	201	-206
22	46	-39
23	49	-45
24	26	20
25	57	61
0 3 L		
0	274	281
1	39	-23
2	102	-91
3	82	71
4	183	-184
5	44	-40
6	193	188
8	41	20
9	62	-59
10	167	-175
11	50	41
12	117	106
14	93	86
15	52	42
16	161	-152
17	41	-29
18	37	32
20	87	86
21	35	-26
22	55	-58
24	31	-31
0 4 L		
0	109	-93
1	55	-27
2	291	-289
3	292	-308
4	320	372
5	309	-364
6	114	-100
7	207	208
8	264	269
9	311	370
10	125	-125
12	51	-40
13	70	-63
14	222	-225
15	73	-67
16	187	179
17	175	-176
20	73	67
21	145	164
22	27	-26
23	34	39
24	17	12
0 5 L		
0	117	-118
1	162	-170
4	108	102
5	110	113
6	51	-45
9	111	-114
11	116	136
12	73	-66
13	49	-49
15	82	-77
16	85	82
17	60	43
19	57	-53
21	69	-64
0 6 L		
0	447	486
2	69	-62
4	70	-75
6	180	-188
10	140	-147
12	249	292
14	83	77
16	62	-57
18	123	-126
20	46	32
0 7 L		
0	41	-44
1	41	29
3	42	29
4	43	33
5	138	-136
6	81	-62
7	109	94
9	58	46
10	75	68
11	54	-49
13	48	-37
14	52	-31
15	66	70
0 8 L		
0	45	-33
1	39	-32
2	82	-72
3	75	66
4	112	115
5	111	113
6	58	-46
7	56	-54
8	80	74
9	112	-115
10	37	-28
11	30	17
0 9 L		
0	81	85
1	25	-18
2	24	-18
3	40	37
4	47	-53
5	25	-24
6	37	44
1 1 L		
0	252	291
2	112	-108
4	231	-216
6	241	242
10	182	-192
12	134	108
14	103	99
16	179	-179
18	45	38
20	100	91
22	70	-59
24	43	-33
26	63	76
1 2 L		
0	158	-151
1	219	223
2	56	39
3	45	28
4	116	117
5	183	-182
6	95	-86
7	78	67
9	132	134
10	80	77
11	164	-182
12	87	-81
13	44	29
15	128	115
16	87	83
17	68	-67
19	54	-55
20	65	-67
21	93	90
22	34	32
23	36	-32
25	40	-41
1 3 L		
0	118	-105
1	158	-153
2	55	54
3	63	-65
4	65	67
5	185	185
6	100	-99
7	99	-105
9	90	-90
10	98	106
11	129	148
12	59	-52
14	43	-21
15	118	-118
16	42	45
17	83	68
20	51	-57
21	68	-75
22	47	47
23	30	25
25	35	53
1 4 L		
0	202	190
2	74	-74
3	66	-53
4	135	-140
5	44	31
6	148	166
9	53	45
10	132	-138
12	71	72
14	67	64
15	43	-33
16	127	-125
17	34	23
18	31	32
20	72	74
21	26	21
22	43	-47
1 5 L		
1	127	141
2	45	41
3	42	37
4	52	55
5	92	-100
6	54	-55
7	38	38
8	33	-29
9	66	69
10	58	59
11	111	-126
12	52	-50
15	100	84
16	58	50
17	44	-37
19	39	-36
20	49	-50
21	48	56
1 6 L		
0	61	-45
1	73	-62
2	28	30
3	48	-52
4	29	30
5	121	122
6	77	-70
7	87	-83
9	29	-38
10	78	72
11	81	76
13	25	28
15	80	-81
17	41	45
1 7 L		
0	68	75
2	39	-38
3	23	-25
4	80	-75
6	90	108
10	72	-71
12	31	25
14	31	31
15	18	-17
1 8 L		
0	45	-43
1	79	82
2	28	15
4	27	34
5	39	-38
6	21	-27
9	39	41
10	23	20
2 2 L		
0	779	977
2	79	-82
4	126	-133
6	415	-451
10	207	-229
12	449	538
14	134	120
16	77	-82
18	219	-226
20	66	54
22	110	-103
24	93	97
2 3 L		
0	82	-75
1	101	85
2	42	32
3	64	54
4	64	58
5	199	-205
6	111	-106
7	133	138
9	83	79
10	103	108
11	101	-105
14	47	-39
15	110	110
16	37	23
17	81	-73
18	30	-21
20	45	-39
21	63	63
22	51	56
23	18	-19
2 4 L		
0	77	-69
2	223	-197
3	227	204
4	257	268
5	258	262
6	88	-81
7	150	-143
8	226	190
9	246	-270
10	103	-85
12	55	-33
13	54	38
14	178	-169
15	64	44
16	147	136
17	133	137
20	50	50
21	115	-134
22	20	-15
2 5 L		
0	163	164
2	51	-47
3	73	63
4	99	-100
5	42	-39
6	95	94
9	53	-56
10	104	-106
11	43	40
12	72	66
14	57	49
15	46	44
16	84	-85
17	28	-31
20	42	58
2 6 L		
2	110	-98
3	105	-89
4	157	144
5	158	-157
6	59	-63
7	83	87
8	112	102
9	143	146
10	38	-33
13	32	-23
14	111	-100
16	76	80
17	73	-90
2 7 L		
0	70	-60
1	•106	-89
4	49	49
5	48	48
9	62	-65
11	72	72
12	37	-35
2 8 L		
0	158	160
2	38	-35
4	35	-29
3 3 L		
0	141	134
2	71	-64
4	138	-130
6	162	178
10	105	-115
12	33	46
14	55	57
16	122	-121
18	45	38
20	66	67
22	30	-37
3 4 L		
0	91	-87
1	151	143
4	86	76
5	88	-81
9	91	87
11	109	-117
12	61	-50
13	29	41
15	70	65
16	66	66
17	36	-31
18	22	9
19	45	-51
20	35	-44
3 5 L		
0	62	-58
1	79	-83
2	44	43
3	51	-45
5	85	85
6	49	-47
7	55	-49
8	38	-28
9	40	-36
10	61	65
11	77	87
12	25	-29
15	76	-73
17	30	30
3 6 L		
0	89	94
2	36	-38
3	41	-43
4	67	-62
6	81	75
9	42	39
10	57	-72
11	35	-28
12	39	38
3 7 L		
0	35	-44
1	62	63
2	24	29
3	23	22
5	37	-42
6	20	-20
7	15	17
8	20	-22
4 4 L		
0	324	360
2	73	-55
4	62	-57
6	148	-125
10	118	-122
12	212	221
14	57	61
16	40	-46
18	75	-97
4 5 L		
0	36	-32
1	33	24
2	23	13
3	36	36
5	107	-111
6	64	-54
7	70	79
9	35	29
10	58	55
11	47	-40
13	35	-33
14	25	-24
5 5 L		
0	50	42
2	29	-21
4	63	-64
6	77	94
10	36	-46

The refinement results were confirmed by a three-dimensional difference Fourier synthesis. The greatest disagreement, situated in the neighbourhood of the bismuth atom, corresponded to 6 electrons/Å^3, a value which is considered acceptable, in view of the high scattering powers of all atoms in $Cs_2Bi_3I_9$.

DISCUSSION OF THE STRUCTURE

The structure of caesium bismuth iodide, $Cs_3Bi_2I_9$, is very closely related to that of $K_3W_2Cl_9$,[10,11] which is representative for the $K7_1$-type structures.[12] The difference between the two structures is that $K_3W_2Cl_9$ has the lower

Table 4. Distances and angles within the $Bi_2I_9^{3-}$ ion.

Bi—Bi	4.051 ± 0.005 Å
$Bi—I_1$	2.923 ± 0.004 Å
$Bi—I_2$	3.249 ± 0.005 Å
$Bi—I_2—Bi$	77.12 ± 0.15°
$I_1—Bi—I_1$	94.13 ± 0.11°
$I_1—Bi—I_2$	90.11 ± 0.11°
$I_1—Bi—I_2'$	173.73 ± 0.13°
$I_2—Bi—I_2$	85.25 ± 0.11°

symmetry of $P6_3/m$. However, the arrangement of the atoms in the two compounds is very similar. This may be seen, if the values of Table 2 in this paper are compared with the refined fractional co-ordinates of $K_3W_2Cl_9$:[13]

4 W in $P6_3/m$:4(*f*) * with $z = 0.176$,
4 K » » » $z = 0.572$,
2 K in $P6_3/m$:2(*a*),
12 Cl in $P6_3/m$:12(*i*) with $x = 0.135$, $y = 0.351$, $z = 0.091$ and
6 Cl in $P6_3/m$:6(*h*) with $x = 0.553$, $y = 0.012$.

A characteristic feature of the $K7_1$-type structures is the presence of distinct $M_2X_9^{3-}$ ions, and it was supposed by Cavalca *et al.*[2] that this might be the case in $Cs_3Bi_2I_9$. The configuration of the $Bi_2I_9^{3-}$ ion, as found in this investigation, is that of two nearly regular iodine octahedra sharing a face, each octahedron having a bismuth atom at its centre (*cf.* Fig. 1). The $Bi—I_2$ distance is 0.31 Å longer than that of $Bi—I_1$ (*cf.* Table 4), which is in accordance with the fact that I_2 is bonded to two Bi atoms, whereas I_1 is attached to only one. In the $W_2Cl_9^{3-}$ ion this difference is not so accentuated, only being 0.08 Å.[13] There is also a great difference between the M—M distance in the $W_2Cl_9^{3-}$ and $Bi_2I_9^{3-}$ ions. The short W—W distance of 2.409 Å indicates

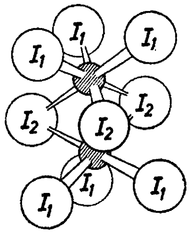

Fig. 1. The configuration of the $Bi_2I_9^{3-}$ ion.

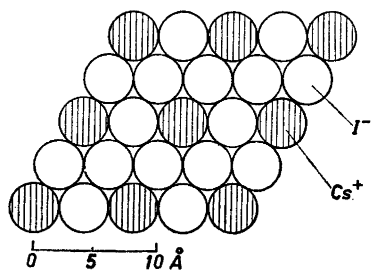

Fig. 2. Part of a close packed layer of caesium and iodine atoms in $Cs_3Bi_2I_9$.

* 2(*a*): ±(0,0,1/4);
4(*f*): ±(1/3,2/3,*z*), ±(1/3,2/3,1/2−*z*);
6(*h*): ±(*x*,*y*,1/4), ±(−*y*,*x*−*y*,1/4), ±(*y*−*x*,−*x*,1/4);
12(*i*): ±(*x*,*y*,*z*), ±(−*y*,*x*−*y*,*z*), ±(*y*−*x*,−*x*,*z*), ±(−*x*,−*y*,1/2+*z*), ±(*y*,*y*−*x*,1/2+*z*), ±(*x*−*y*,*x*,1/2+*z*);

Table 5. Distances and angles within the caesium-iodine co-ordination polyhedra (*cf.* Fig. 3).

$I_2 - Bi$	3.249 ± 0.005 Å	$I_1 - Bi$	2.923 ± 0.004 Å
$I_2 - Cs_{11,12}$	4.242 ± 0.007 Å	$I_1 - Cs_{11}$	4.244 ± 0.007 Å
$I_2 - Cs_{21,22}$	4.205 ± 0.010 Å	$I_1 - Cs_{12,13}$	4.206 ± 0.007 Å
$I_2 - I_{11,12,13,14}$	4.377 ± 0.005 Å	$I_1 - Cs_{21}$	4.308 ± 0.004 Å
$I_2 - I_{21,22}$	4.401 ± 0.010 Å	$I_1 - I_{11,12}$	4.168 ± 0.007 Å
$I_2 - I_{23,24}$	4.010 ± 0.010 Å	$I_1 - I_{13,14}$	4.132 ± 0.005 Å
		$I_1 - I_{15,16}$	4.280 ± 0.005 Å
$I_{21,23} - I_2 - I_{22,24}$	60.00° ± 0.07°	$I_1 - I_{21,22}$	4.377 ± 0.005 Å
$Cs_{21,22} - I_2 - I_{21,22}$	58.46° ± 0.08°		
$Cs_{21,22} - I_2 - I_{24,23}$	61.54° ± 0.08°	$Cs_{12,13} - I_1 - I_{13,15}$	60.58° ± 0.07°
$Cs_{11,12,11,12} - I_2 - I_{23,23,24,24}$	61.79° ± 0.08°	$Cs_{12,13} - I_1 - I_{16,14}$	59.42° ± 0.09°
$Cs_{21,22,21,22} - I_2 - I_{11,12,13,14}$	60.23° ± 0.08°	$I_{13,15} - I_1 - I_{14,16}$	60.00° ± 0.07°
$I_{21,22,21,22} - I_2 - I_{11,12,13,14}$	59.80° ± 0.10°	$Cs_{12,13} - I_1 - I_{11,12}$	60.90° ± 0.10°
$Cs_{11,11,12,12} - I_2 - I_{11,12,13,14}$	58.40° ± 0.06°	$I_{15,16} - I_1 - Cs_{11,11}$	59.72° ± 0.07°
$I_{11,12} - I_2 - I_{13,14}$	58.55° ± 0.08°	$Cs_{11,11} - I_1 - I_{11,12}$	59.99° ± 0.09°
		$I_{13,14} - I_1 - I_{11,12}$	60.29° ± 0.07°
		$I_{11} - I_1 - I_{12}$	59.42° ± 0.11°
$Cs_1 - I_{11,12,13}$	4.244 ± 0.007 Å	$Cs_{12,13} - I_1 - I_{21,22}$	59.19° ± 0.12°
$Cs_1 - I_{14,15,16,17,18,19}$	4.206 ± 0.007 Å	$Cs_{21,21} - I_1 - I_{13,14}$	61.34° ± 0.07°
$Cs_1 - I_{21,22,23}$	4.242 ± 0.007 Å	$Cs_{21,21} - I_1 - I_{21,22}$	57.93° ± 0.08°
		$I_{15,16} - I_1 - I_{22,21}$	60.70° ± 0.09°
$I_{14,16,18} - Cs_1 - I_{15,17,19}$	58.83° ± 0.10°	$I_{21} - I_1 - I_{22}$	60.38° ± 0.14°
$I_{15,17,17} - Cs_1 - I_{16,18,14}$	61.16° ± 0.07°		
$I_{11,12,13} - Cs_1 - I_{12,13,11}$	60.56° ± 0.12°		
$I_{21,22,23} - Cs_1 - I_{22,23,21}$	56.43° ± 0.15°	$Cs_2 - I_{11,12,13,14,15,16}$	4.308 ± 0.004 Å
$I_{11} - Cs_1 - I_{14}$ (6x)	59.10° ± 0.09°	$Cs_2 - I_{21,22,23,24,25,26}$	4.205 ± 0.006 Å
$I_{21} - Cs_1 - I_{14}$ (6x)	62.41° ± 0.10°		
		$I_{21,23,25} - Cs_2 - I_{22,24,26}$	56.93° ± 0.16°
		$I_{22,24,26} - Cs_2 - I_{23,25,21}$	63.07° ± 0.16°
		$I_{11} - Cs_2 - I_{12}$ (6x)	57.32° ± 0.09°
		$I_{11} - Cs_2 - I_{21}$ (12x)	61.84° ± 0.05°

a W—W double bond,[13] whereas the corresponding Bi—Bi distance of 4.051 Å shows no such signs.

The caesium ions are situated between the $Bi_2I_9^{3-}$ ions in such a way as to give a nearly ideal hexagonal-type close packing of the caesium and iodine atoms. Each layer in the close packing has the same configuration, with three iodine atoms for each caesium, as shown in Fig. 2. The layers, which are perpendicular to the *c* axis, are in sequence ABACBCAB . . . throughout the whole structure.

The distances and angles within the co-ordination polyhedra of caesium and iodine are given in Table 5, the notations of which are in accordance with Fig. 3. The mean value of the intermolecular I—I distances in $Cs_3Bi_2I_9$ is 4.15 Å, which is shorter than the corresponding values for CsI_3 and NH_4I_3 of 4.34 Å and 4.28 Å, respectively.[14] The average distance between the caesium and iodine atoms in $Cs_3Bi_2I_9$ is 4.24 Å. This is longer than in CsI (3.95 Å),[15,16] as expected from the different co-ordination numbers (12 in $Cs_3Bi_2I_9$ and 8 in CsI). It is also longer than the average Cs—I distance found in Cs_2I_9 (4.05 Å) [17] for the same reason (co-ordination number 10).

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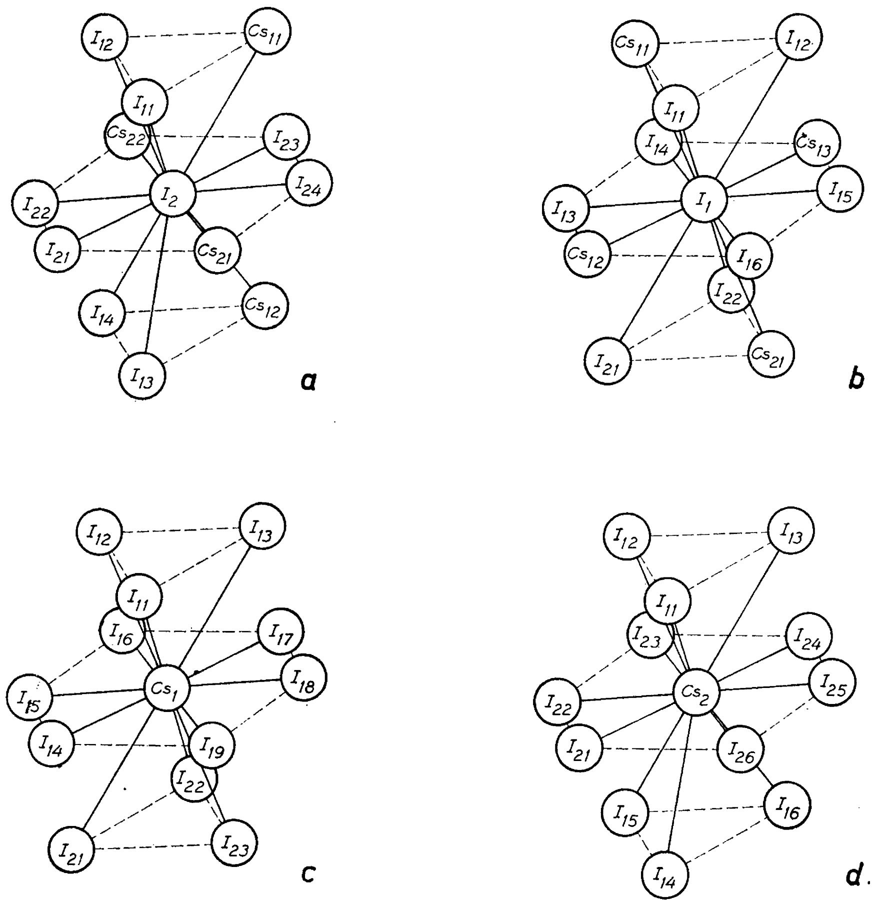

Fig. 3. Co-ordination polyhedra of the caesium and iodine atoms. In a, I_{11}, I_{12}, I_{13}, I_{14}, I_{21} and I_{22} belong to the same $Bi_2I_9^{3-}$ ion as I_2 and in b, I_{13}, I_{14}, I_{21}, and I_{22} belong to the same group as I_1.

that time worked at the Department of Analytical Chemistry at this University. The drawings have been made by Ing. Ingrid Ingvarsson, and the English text has been revised by Dr. Andrew Jelen.

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