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1.

THE STRUCTURE OF WHITE CESIUM LEAD(II) BROMIDE, $CsPbBr_3$

BY

ASTRID MARSTRANDER AND
CHRISTIAN KNAKKERGÅRD MØLLER

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Synopsis

Crystals of the white modification of $CsPbBr_3$ – contaminated with orange crystals of the same composition – can be obtained from aqueous solutions of CsBr and $PbBr_2$. The white crystals appear to be only slightly less stable than the orange ones. They are needle-shaped with γ' parallel with the needle axis and they undergo a phase transition to the orange modification at 130° C. The *X*-ray analysis shows that the white crystals are orthorhombic belonging to space group no. 62 Pmnb, and $a = 4.597$ Å, $b = 9.72$ Å, $c = 16.81$ Å. The structure is quite analogous to that of the yellow $CsPbI_3$. Distorted $PbBr_6$-octahedra sharing Br-atoms form chain-like, polynuclear ions $(PbBr_3^-)_n$ running parallel with the *a*-axis. The Pb-Br-distances vary from 2.82 Å to 3.29 Å.

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Introduction

It has been shown previously that $CsPbI_3$ exists in two modifications, a black metastable form with perovskite structure and a yellow orthorhombic form which is stable under ordinary conditions[1]. $CsPbBr_3$ apparently also exists in two forms, an orange-coloured form with perovskite structure, which already has been investigated[2], and the supposed analogue of the yellow orthorhombic $CsPbI_3$, which has been prepared by WELLS and co-workers[3].

Although a fairly complete *X*-ray analysis has been done on the orthorhombic $CsPbI_3$, it seemed worth while to make an independent investigation of the white $CsPbBr_3$ in order to check the irregular octahedral coordination of the halogen atoms around the lead atoms which was found in the former compound. Also, in the previous investigation no distinction could be made between the halogen atoms and the cesium atoms because of their equal scattering powers. And finally, it might be interesting to see if the atomic parameters would be the same as in $CsPbI_3$ in spite of differences in absorption and dispersion effects.

Preparation and properties of the white $CsPbBr_3$-crystals

We have obtained the white modification of $CsPbBr_3$ in the following way. First CsBr was prepared from Cs_2CO_3 and an aqueous solution of HBr. $PbBr_2$ was precipitated from aqueous solutions of $Pb(NO_3)_2$ and HBr, recrystallized a few times in hot water. All the chemicals were Riedel-de Haën pro analysi.

Aqueous solutions with well-defined concentrations of CsBr were next prepared and saturated with $PbBr_2$ by boiling. Undissolved $PbBr_2$ was separated from the still hot solutions. On addition of an amount of hot or cold water to each solution so that the CsBr-concentrations as well as the

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[1] C. K. MØLLER, The Structure of $CsPbI_3$. Mat. Fys. Medd. Dan. Vid. Selsk. **32** No. 1 (1959).

[2] C. K. MØLLER, The Structure of Perovskite-like Cæsium Plumbo Trihalides. Mat. Fys. Medd. Dan. Vid. Selsk. **32** No. 2 (1959).

[3] H. L. WELLS, Z. anorg. Chem. **3**, 195 (1893).

temperatures were kept within a certain range a precipitation of crystals usually resulted.

White needle-shaped crystals were obtained when the final concentration of CsBr was in the range 23.5–27.5 g CsBr/100 g H_2O, and the temperature at which they appeared was usually 23–25° C; but they were always contaminated with orange crystals, and sometimes also with thin flaky crystals (of $CsPb_2Br_5$?), the latter ones, however, disappearing after some time.

To avoid the formation of basic salts the solutions were mostly kept acid with pH = 1–3. Higher pH-values seemed to change the conditions for precipitation of the white crystals of $CsPbBr_3$ in the direction of higher CsBr-concentrations. Supersaturated solutions easily resulted so that seeding often was necessary.

Sometimes very thin needles of white crystals $\frac{1}{2}$ – 1 cm long were obtained. Apparently they grew very quickly under special conditions.

Only by hand-sorting under a microscope was it possible to obtain a pure product of white crystals—free from orange-coloured contaminations.

Under the polarizing microscope these crystals showed extinction parallel with and perpendicular to the needle-axis. When heated under the microscope on a hot stage the white crystals changed irreversibly into the orange modification at 130° C—this temperature being about 10° C lower than that mentioned by WELLS[1].

The *X*-ray work to be mentioned shows that the crystals have the stoichiometric composition $CsPbBr_3$ as found by WELLS et al[1].

Stability of the white $CsPbBr_3$-crystals

From the observation that the white needle-shaped crystals and the orange crystals could co-exist at room temperature (18–20° C) for months in aqueous solutions of CsBr with concentrations as mentioned above, it would appear that there can be only a small difference in free energy between the two forms. The white crystals eventually slowly disappeared and only orange-coloured crystals were left. With crystals of the same composition the CsBr-concentration of the solution would not be expected to influence the relative stability of the two forms, and hence it is concluded that the orange crystals are slightly more stable than the white ones. When dry, the white crystals can be kept at room temperature indefinitely.

An attempt was made to measure the difference in free energy between the two modifications. Electrochemical cells of the following type were constructed:

$$\mathrm{Pt} \,|\, \mathrm{Pb(Hg)} \,|\, \mathrm{CsPbBr_3(orange)} \,|\, \text{solution } 27\,\mathrm{g}\ \mathrm{CsBr}/100\,\mathrm{g}\ \mathrm{H_2O} \,|\, \mathrm{CsPbBr_3(white)} \,|\, \mathrm{Pb(Hg)} \,|\, \mathrm{Pt}.$$

They were kept at temperatures 19.5°C or 22.5°C. However, it was difficult to obtain reliable values for the emf.'s of the cells. Shortly after assemblage the cell had an emf. of 2–3 mv, but then drifted slowly towards lower values. Only on one occasion did the emf. stay within the interval 2.5–3.0 mv the first 24 hours after construction of the cell.

The electrode with the white $CsPbBr_3$-crystals was the positive electrode, suggesting the electrode processes:

$$2\,e^- + \mathrm{CsPbBr_3}\ (\text{white}) \rightarrow \mathrm{Cs^+} + 3\ \mathrm{Br^-} + \mathrm{Pb}$$

$$\mathrm{Cs^+} + 3\ \mathrm{Br^-} + \mathrm{Pb} \rightarrow \mathrm{CsPbBr_3}\ (\text{orange}) + 2\,e^-$$

Hence the white crystals are less stable than the orange ones. If a value of c. 3 mv for the emf. is accepted as being significant, the corresponding difference in free energy is $\Delta G = 3 \cdot 10^{-3} \cdot 96000 \cdot 2 \sim 600$ Joule or 140 cal/mole, which is quite small.

X-ray investigation

Oscillation and Weissenberg diagrams of single crystals of the white $CsPbBr_3$-compound showed that they had orthorhombic symmetry, and preliminary values for the crystal axes were determined from these photographs. Refined values were obtained from powder photographs in a Guinier type focusing camera as previously described[1], and Table 1 shows a comparison of the observed $\sin^2\theta$-values with those calculated from the finally accepted unit cell axes:

$$a = 4.597 \pm 0.005\,\text{Å}, \quad b = 9.72 \pm 0.01\,\text{Å}, \quad c = 16.81 \pm 0.02\,\text{Å}.$$

From the similarity of the powder patterns of the yellow $CsPbI_3$ and of the white $CsPbBr_3$ it is concluded that the two compounds are isomorphous with the same number of molecules in the unit cell, i. e. 4. On this basis and with the unit cell axes given above the molar volume for white $CsPbBr_3$ is 113.7 cc. This may be compared with the molar volume 120.5 cc for the orange modification and a value of 103.0 calculated from the molar volumes of CsBr and $PbBr_2$. We thus find the same trend as for the analogous iodides[4].

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[4] C. K. Møller, The Structure of Cæsium Hexahalogeno-Plumbates(II). Mat. Fys. Medd. Dan. Vid. Selsk. **32** No. 3, p. 6 (1960).

TABLE 1. Observed and calculated $\sin^2\theta$-values for white $CsPbBr_3$. CuK_α-radiation.

Indices	Estimated intensity	$10^4 \times \sin^2\theta_{obs}$	$10^4 \times \sin^2\theta_{calc}$
011	m-w	0083	0084
002			0084
012	w	0148	0147
020	w	0252	0252
013			0252
021	m-w	0272	0273
111	s	0364	0365
014	m	0401	0399
112	m-w	0426	0428
023	w	0441	0441
120	m-w	0532	0533
113			
121	m	0555	0554
015	w	0589	0589
024			0588
031			0588
122	s	0616	0617
032	vw	0653	0651
123	vw	0721	0722
105	m	0809	0807
016	vw	0820	0820
115	vw	0869	0870
124			0869
131			0869
132	w	0932	0932
200	m-w	1125	1125
134	w	1187	1184
212	vw	1270	1272
126	w	1294	1290
117	s	1377	1375
213			1377
220			1377
224	vw	1716	1713
215			1714

TABLE 2. Atomic parameters in white $CsPbBr_3$.

All the atoms are in the special positions:

$$\frac{1}{4}yz;\quad \frac{3}{4}\bar{y}\bar{z};\quad \frac{3}{4}\,\frac{1}{2}-y\;\frac{1}{2}+z;\quad \frac{1}{4}\,\frac{1}{2}+y\;\frac{1}{2}-z$$

and for

Cs	$x = \frac{1}{4}$	$y = 0.089$	$z = 0.329$
Pb	$x = \frac{3}{4}$	$y = 0.163$	$z = 0.063$
Br′	$x = \frac{1}{4}$	$y = 0.335$	$z = 0.000$
Br″	$x = \frac{3}{4}$	$y = 0.028$	$z = \overline{0.116}$
Br‴	$x = \frac{3}{4}$	$y = 0.302$	$z = 0.211$

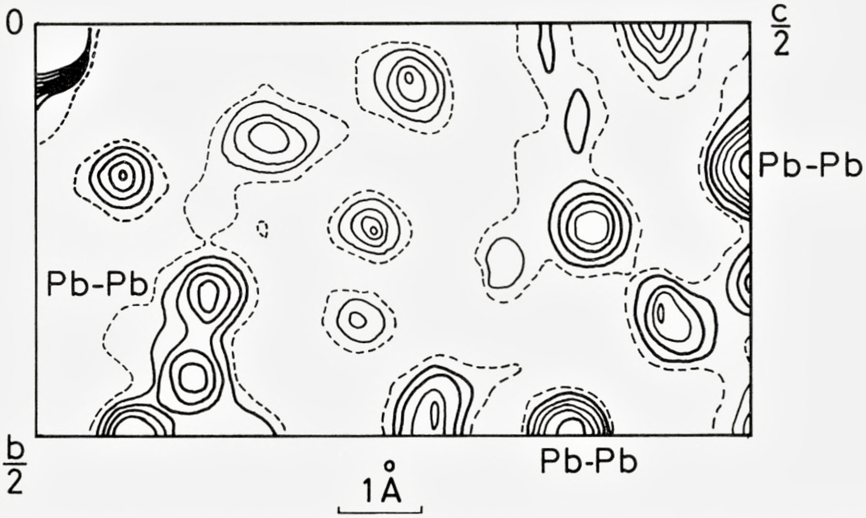

Fig. 1. Patterson projection of the white $CsPbBr_3$ on (100). Contours are drawn at the relative densities 0 (dashed), 25, 50, 75, 100, 150 and 200.

In order to see if there should be any relation between lattice planes in the orange and the white modifications of $CsPbBr_3$, oscillation diagrams were taken of a single crystal of white $CsPbBr_3$. Then the crystal was heated in a controlled flow of hot N_2-gas and thus partly converted to the orange modification while another oscillation diagram was taken. The latter shows a powder pattern superimposed on an oscillation diagram of white $CsPbBr_3$, but apparently there is no simple connection between "old" and "new" *X*-ray reflections, and it appears that the crystal is converted into a disordered powder of orange $CsPbBr_3$ within the boundary of the original crystal.

With CuK_α-radiation intensities were obtained from Weissenberg exposures by a multiple film technique as previously described[1]. The crystal was rotated about the *a*-axis—which is also the needle axis. Its length was 0.42 mm and the cross section of the crystal 0.035×0.010 mm^2.

Reflections of the type h0l were absent for h+l odd and hk0 were absent for k odd. No other systematic absences were observed, but I(0kl) and I(2kl) appeared to be equal for all values of k and l. As these rules are exactly the same as for yellow $CsPbI_3$, it is inferred that the space group is also the the same, no. 62 Pmnb.

The procedure and the arguments for determining the atomic arrangement from the observed intensities were from now exactly the same as described

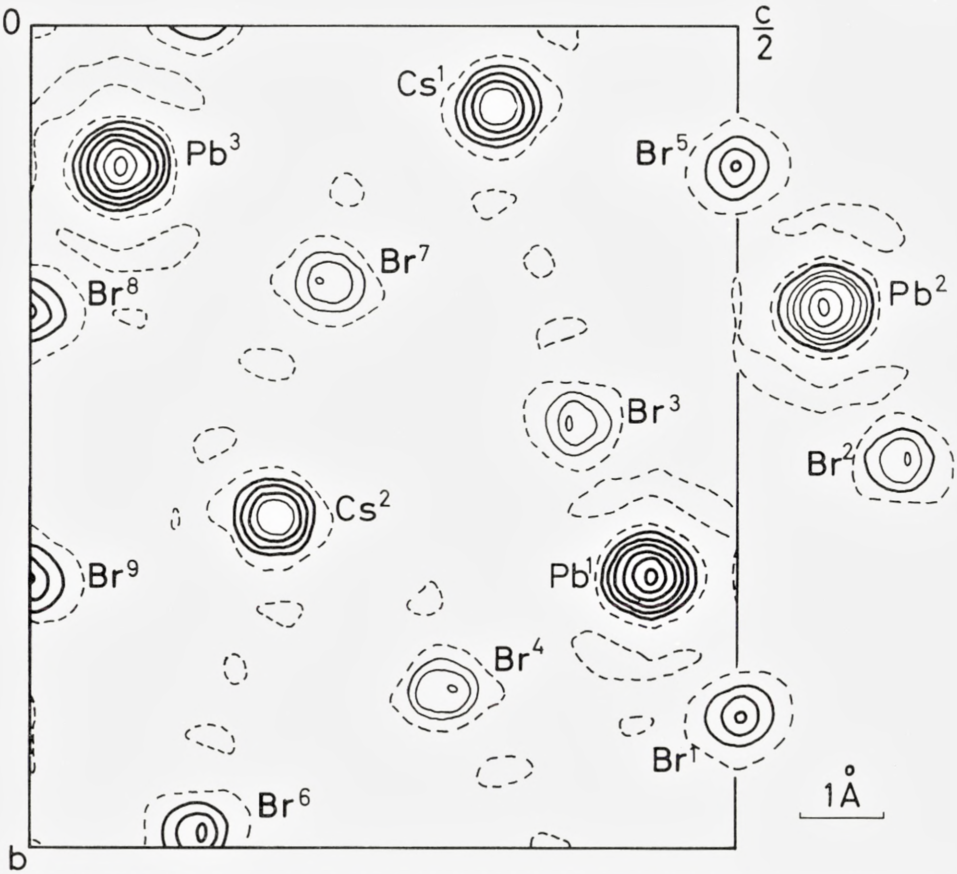

Fig. 2. Electron projection of the white $CsPbBr_3$ on (100). Contours are drawn at the relative densities 0 (dashed), 100, 200, 300, 400, 600 and 800.

for $CsPbI_3$[1] and no detailed account of it will be given. Suffice it to say that the structure of white $CsPbBr_3$ was solved independently of that of the analogous iodide and hence both Patterson and electron projections as well as difference maps were evaluated (figs. 1 and 2). The Fourier syntheses and the structure factors were calculated on a GIER electronic computer using programmes which had originally been worked out by J. Danielsen[5], and atomic scattering factors from Forsyth and Wells' paper[6].

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[5] J. Danielsen, Acta Cryst. **16** Suppl. A 171 (1963).
[6] J. B. Forsyth and M. Wells, Acta Cryst. **12**, 412 (1959).

TABLE 3. Comparison of calculated and observed structure factors for white $CsPbBr_3$ (brought on the same relative scale).

$h\,k\,l$	$\lvert F_{obs}\rvert$	F_{calc}	$h\,k\,l$	$\lvert F_{obs}\rvert$	F_{calc}	$h\,k\,l$	$\lvert F_{obs}\rvert$	F_{calc}
0 0 2	105	+ 85	0 2 15	46	+ 47	0 5 1	79	+ 83
0 0 4	27	− 10	0 2 19	65	− 76	0 5 2	139	+ 164
0 0 6	41	+ 31	0 2 20	23	− 32	0 5 3	74	− 74
0 0 8	144	− 129	0 2 21	10	− 12	0 5 4	108	+ 102
0 010	22	+ 10	0 3 1	22	− 19	0 5 5	77	− 69
0 012	45	+ 46	0 3 2	121	+ 147	0 5 6	58	+ 50
0 014	79	+ 65	0 3 3	84	− 79	0 5 7	12	+ 13
0 016	85	+ 102	0 3 4	128	− 137	0 5 9	122	− 128
0 018	99	+ 130	0 3 5	133	− 138	0 5 10	67	− 66
0 020	16	− 23	0 3 7	149	+ 166	0 5 11	31	+ 26
0 1 1	49	+ 54				0 5 12	65	− 58
0 1 2	85	− 85	0 3 8	31	+ 27	0 5 14	53	− 50
0 1 3	96	+ 77	0 3 9	199	+ 225	0 5 15	39	− 40
0 1 4	166	− 155	0 3 10	40	− 36	0 5 17	75	+ 76
0 1 5	201	− 227	0 3 11	70	+ 62	0 5 18	48	+ 51
0 1 6	170	− 164	0 3 12	40	+ 38	0 6 0	117	+ 133
0 1 7	118	− 94	0 3 13	43	− 39	0 6 1	97	+ 93
0 1 8	108	+ 92	0 3 15	42	− 39	0 6 2	137	+ 165
0 1 9	25	+ 21	0 3 16	41	− 48	0 6 4	68	+ 60
0 1 10	24	+ 17	0 3 17	28	− 25	0 6 6	120	− 118
0 1 11	94	− 94	0 3 19	18	+ 29	0 6 9	35	− 21
0 1 12	115	+ 119	0 3 20	21	+ 31	0 6 11	33	+ 36
0 1 13	42	− 40	0 4 0	114	− 128	0 6 12	41	− 35
0 1 14	79	+ 77	0 4 1	54	− 57			
0 1 15	57	+ 62	0 4 2	77	− 72	0 6 13	26	− 25
0 1 16	51	− 58	0 4 3	161	+ 204	0 6 14	104	+ 114
0 1 17	14	+ 17	0 4 4	47	− 42	0 6 16	84	+ 83
0 1 20	43	− 51	0 4 5	130	+ 133	0 6 18	33	+ 30
0 2 0	59	− 59	0 4 6	52	− 42	0 7 1	82	+ 83
0 2 1	87	− 104	0 4 7	68	− 67	0 7 2	75	− 77
0 2 2	63	− 66	0 4 8	115	+ 108	0 7 3	82	− 77
0 2 3	130	− 155	0 4 10	67	+ 55	0 7 6	122	− 115
0 2 4	138	− 156	0 4 11	56	− 53	0 7 7	89	− 82
0 2 5	72	− 54	0 4 12	90	− 90	0 7 9	77	− 76
0 2 6	63	+ 54	0 4 13	76	− 78	0 7 10	96	+ 95
0 2 7	149	− 148	0 4 14	39	− 34	0 7 12	71	+ 63
0 2 8	93	+ 76	0 4 15	47	− 42	0 7 17	30	+ 30
0 2 9	73	+ 58	0 4 16	50	− 44	0 8 0	92	− 87
0 2 10	12	+ 1	0 4 17	42	+ 51	0 8 1	35	+ 25
0 2 11	162	+ 181	0 4 18	33	− 37	0 8 3	48	− 45
0 2 14	104	− 117	0 4 19	23	+ 26	0 8 4	33	− 29

TABLE 3 (continued)

$h\,k\,l$	$\lvert F_{\text{obs}}\rvert$	F_{calc}	$h\,k\,l$	$\lvert F_{\text{obs}}\rvert$	F_{calc}	$h\,k\,l$	$\lvert F_{\text{obs}}\rvert$	F_{calc}
0 8 5	131	− 141	1 1 2	77	+ 76	1 3 8	28	− 21
0 8 7	24	− 7	1 1 3	153	− 144	1 3 9	90	− 94
0 8 8	43	+ 37	1 1 5	43	− 33	1 3 10	91	+ 94
0 8 9	39	+ 34	1 1 6	133	+ 122	1 3 11	61	+ 61
0 8 11	57	+ 43	1 1 7	213	− 230	1 3 12	73	+ 80
0 8 13	98	+ 97	1 1 8	123	+ 105	1 3 14	68	+ 70
0 8 14	33	− 35	1 1 9	160	− 160	1 3 15	50	− 60
0 8 15	24	− 28	1 1 10	164	− 183	1 3 16	38	+ 38
0 9 1	63	− 53	1 1 11	77	− 63	1 3 17	55	+ 74
0 9 3	20	+ 22	1 1 12	76	− 64	1 3 18	77	− 88
0 9 5	44	+ 44	1 1 14	31	+ 30	1 3 20	44	− 58
0 9 7	97	+ 92	1 1 15	38	+ 34	1 4 0	133	− 176
0 9 8	64	− 65	1 1 16	19	− 27	1 4 2	130	− 154
0 9 9	93	+ 90	1 1 17	40	+ 38	1 4 3	129	− 146
0 9 10	80	+ 82	1 1 18	41	+ 44	1 4 4	33	− 23
0 9 14	32	− 31	1 1 19	26	+ 18	1 4 5	103	− 103
010 1	59	+ 60	1 1 20	16	+ 19	1 4 6	58	− 52
010 2	96	− 90	1 1 21	41	− 80	1 4 7	74	+ 67
010 3	74	+ 66	1 2 0	87	+ 106	1 4 8	114	+ 125
010 6	57	+ 48	1 2 1	132	− 204	1 4 10	92	+ 90
010 10	20	+ 19	1 2 2	200	+ 304	1 4 12	118	− 146
011 1	23	− 21	1 2 3	91	− 91	1 4 13	77	+ 80
011 2	58	+ 46	1 2 4	63	+ 56	1 4 14	35	− 31
011 3	52	+ 47	1 2 5	31	− 20	1 4 15	30	+ 30
011 4	80	+ 79	1 2 6	158	− 155	1 4 16	79	− 92
011 5	35	− 39	1 2 7	31	− 23	1 4 17	34	− 35
011 7	25	− 27	1 2 9	59	+ 52	1 4 18	53	− 65
011 10	25	− 25	1 2 10	41	− 30	1 4 19	21	− 25
012 0	67	+ 74	1 2 13	52	+ 46	1 5 1	34	− 26
012 2	43	+ 45	1 2 14	97	+ 117	1 5 2	100	− 99
			1 2 15	31	+ 33	1 5 3	57	− 55
1 0 1	21	− 18	1 2 16	102	+ 125	1 5 4	150	+ 178
1 0 3	103	+ 67	1 2 18	27	+ 29	1 5 5	77	+ 81
1 0 5	291	+ 332	1 2 19	54	− 71	1 5 7	152	+ 179
1 0 7	46	+ 24	1 2 20	26	+ 40	1 5 9	128	+ 139
1 0 9	99	− 89	1 3 1	80	+ 86	1 5 11	76	+ 77
1 0 11	76	− 69	1 3 2	141	− 175	1 5 12	66	− 68
1 0 13	171	− 210	1 3 3	105	− 111	1 5 13	38	− 30
1 0 15	55	+ 65	1 3 4	176	− 222	1 5 14	36	− 29
1 0 17	55	+ 58	1 3 5	18	− 2	1 5 15	64	− 60
1 0 21	43	+ 73	1 3 6	14	− 7	1 5 16	32	+ 42
1 1 1	98	+ 154	1 3 7	66	+ 64	1 6 1	111	+ 131

TABLE 3 (continued)

$h\,k\,l$	$\|F_{obs}\|$	F_{calc}	$h\,k\,l$	$\|F_{obs}\|$	F_{calc}	$h\,k\,l$	$\|F_{obs}\|$	F_{calc}
1 6 2	27	+ 21	1 7 15	59	+ 64	1 9 13	21	− 24
1 6 3	79	+ 80	1 7 16	46	+ 53	1 9 14	38	+ 44
1 6 4	80	− 75	1 7 17	10	+ 6	1 10 1	24	− 24
1 6 5	74	+ 66	1 8 0	208	+ 258	1 10 2	80	− 81
1 6 7	123	+ 132	1 8 1	43	− 35	1 10 3	63	− 61
1 6 8	54	+ 48	1 8 2	60	+ 53	1 10 4	62	− 60
1 6 9	72	− 76	1 8 5	57	− 50	1 10 6	37	+ 38
1 6 11	119	− 133	1 8 8	72	− 68	1 10 7	52	− 51
1 6 13	36	− 29	1 8 12	35	+ 39	1 10 8	38	+ 38
1 6 14	66	− 62	1 8 13	48	+ 53	1 10 9	23	+ 14
1 7 1	62	− 62	1 8 14	29	+ 28	1 10 10	27	+ 19
1 7 4	94	+ 90	1 9 2	49	− 50	1 10 11	74	+ 82
1 7 5	103	− 109	1 9 3	62	+ 62	1 11 2	56	+ 55
1 7 6	85	+ 79	1 9 4	98	− 95	1 11 3	30	− 23
1 7 7	121	− 132	1 9 5	98	− 101	1 11 5	41	+ 44
1 7 8	61	− 58	1 9 6	59	− 58	1 11 7	56	+ 61
1 7 11	86	− 90	1 9 9	38	+ 35	1 11 8	29	+ 33
1 7 12	67	− 73	1 9 10	33	+ 34	1 11 9	69	+ 107
1 7 13	33	− 30	1 9 11	24	− 33	1 12 0	37	− 30
1 7 14	44	− 49	1 9 12	66	+ 68	1 12 3	56	+ 74

TABLE 4. Interatomic distances in white $CsPbBr_3$.

Distance	From this investigation	From Pauling's ionic radii	From Goldschmidt's radii
Pb^1-Br^1	3.04 Å	3.16 Å	3.28 Å
Pb^1-Br^2	3.29 -		
Pb^1-Br^3	3.08 -		
Pb^1-Br^4	2.82 -		
Pb^1-Pb^2	4.46 -		
Pb-Cs	5.08 -		
Cs^1-Br^5	3.76 -	3.64 -	3.63 -
Cs^1-Br^1	3.79 -		
Cs^1-Br^6	3.75 -		
Cs^1-Br^3	3.84 -		
Cs^1-Br^4	3.67 -		
Cs^1-Br^7	3.67 -		
Br^1-Br^1	4.60 -		
Br^1-Br^2	4.24 -		
Br^1-Br^3	4.03 -		
Br^1-Br^4	4.24 -		

Structure factors which have been calculated from the atomic parameters in Table 2 are compared with the observed values in Table 3 after they have been brought on the same relative scale. Interatomic distances obtained with these parameters are given in Table 4.

Conclusion

The structure of the white $CsPbBr_3$ as determined from the present work is in complete analogy with that of the yellow $CsPbI_3$ and exhibits the same kind of irregular octahedral coordination of the halogen atoms around the lead atoms. In both structures catena-ions $(PbX_3^-)_n$ are parallel to the a-axis and the Cs-ions are held between these chain-like ions. One of the lead-halogen distances is considerably shorter than the others and also shorter than the sum of the corresponding ionic radii or Slater atomic radii: 2.82 Å against 3.16 Å or 2.95 Å, respectively. This might indicate a stronger bonding between lead and this particular halogen atom.

The variations of the interatomic distances in the two analogous crystals are also quite similar although the dispersion effects have not been considered in case of the bromide. One might, therefore, be tempted to conclude that if an uncertainty of 0.05 Å on the interatomic distances can be tolerated, the influence of dispersion may be neglected.

Acknowledgements

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[7] J. C. Slater, J. Chem. Phys. **41**, 3199 (1964).

Chemistry Department I, Inorganic Chemistry,
The H. C. Ørsted Institute,
University of Copenhagen, Denmark