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ON THE STRUCTURE OF CÆSIUM HEXAHALOGENO-PLUMBATES (II)

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Synopsis

Crystalline compounds of composition Cs_4PbX_6 , in which $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ may be prepared either from aqueous solutions or by fusing CsX and PbX_2 together. X-ray investigations show that the crystals are rhombohedral and belong to space group No. 167 $R\bar{3}c$. The hexagonal unit cells have dimensions $a = 13.18_7 \text{ \AA}$, $c = 16.64_1 \text{ \AA}$ for Cs_4PbCl_6 ; $a = 13.73_2 \text{ \AA}$, $c = 17.32_4 \text{ \AA}$ for Cs_4PbBr_6 ; $a = 14.52_8 \text{ \AA}$, $c = 18.31_3 \text{ \AA}$ for Cs_4PbI_6 , and contain six "molecules". The molar volumes of Cs_4PbX_6 are larger than the sum of the molar volumes of CsX and PbX_2 by c. 6 cc. per gram-atom halogen. — Atomic parameters can be obtained from fairly well resolved Patterson- and electron-projections on $(1\bar{2}10)$. The Pb- and X-atoms form isolated, slightly distorted PbX_6 -octahedra; the PbCl-distances are 2.93 \AA and the PbBr-distances are 3.12 \AA , i. e. in both cases a little longer than in the CsPbX_3 -compound, but shorter than the sum of the ionic radii. The agreement between calculated and observed structure factors is not so good as wanted. This may in part be due to a small delocalization around their average positions of the Cs-atoms having an irregular 8-coordination.

Introduction

In the course of a systematic study of the structure of the plumbo-halogen complex ions it became of interest also to examine the crystalline compounds with the general formula Cs_4PbX_6 . The interpretation of the Guinier diagram of CsPbCl_3 had already made it necessary to investigate the powder diagram of Cs_4PbCl_6 ¹ and from this start we have continued work on structures of this type. When it had progressed so far that most of the facts mentioned in the present article could materialize it was understood from a footnote in a paper by G. BERGERHOF and O. SCHMITZ-DUMONT² that these authors had also been engaged on the same problem. However, they have not, apparently, published any results of their investigations, and we have therefore taken the opportunity to give an account of our own work on these compounds as they are closely related to the previously investigated structure of type CsPbX_3 .

Preparation and some general properties

The crystalline compounds Cs_4PbCl_6 and Cs_4PbBr_6 can be made in two ways: (1) By dissolving PbX_2 in a boiling aqueous solution which is almost saturated with CsX at room temperature, filtering while still hot and then leave to slow cooling.³ (2) By fusing CsX and PbX_2 together in the correct stoichiometric proportion. — As for Cs_4PbI_6 this compound had not been prepared before; it was obtained (unintentionally) by boiling PbBr_2 in an aqueous solution nearly saturated with a fifty–fifty mixture of CsBr and CsI . It does not seem possible to obtain it in a pure state by melting PbI_2 and CsI together in the stoichiometric proportion: The powder diagrams of such products besides lines of Cs_4PbI_6 invariably also show the presence of

¹ C. K. MØLLER, The Structure of Perovskite-like Cæsium Plumbo Trihalides. *Mat. Fys. Medd. Dan. Vid. Selsk.* **32**, No. 2 (1959).

² G. BERGERHOF u. O. SCHMITZ-DUMONT. *Z. anorg. u. allgem. Chem.* **284**, 10 (1956).

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

CsI-lines. Apart from this the identity of compounds obtained in the different ways was shown from their X-ray powder diagrams.

The crystals grown from solutions were colourless and their most prominent faces were parallelogram-shaped with angles 72° – 60° and 108° – 120° . Under the polarizing microscope the Cl- and Br-compounds showed diagonal extinction with α' bisecting the acute angles. The refractive indices were high, but the birefringence low. On the assumption that the crystals were hexagonal (proved from the X-ray work) it could be inferred from conoscopic examination that they were uniaxially positive in all three cases.

The density was determined on single crystals of Cs_4PbCl_6 by flotation in Clerici solutions of different densities to be $3.70 \pm 0.07 \text{ g/cm}^3$.

No changes of the crystals could be observed on heating them to about 320° C .

Space group and unit cell dimensions

X-ray investigations on powders of Cs_4PbCl_6 , Cs_4PbBr_6 , and Cs_4PbI_6 , and on single crystals of the first two were made along the same lines as in the previous paper (1).

The Weissenberg diagrams taken about twofold axes of the single crystals could be indexed on a hexagonal lattice. Reflections of type $hkil$ were only observed for $-h+k+l=3n$, and $h\bar{h}0l$ only for $l=2n$, so that the space group can be either No. 167 $R\bar{3}c$ or No. 161 $R3c$, but as no piezoelectric effect could be detected by a dynamical method,⁴ the former seems most likely. The Guinier diagrams could be indexed by application of the general quadratic form:

$$\sin^2 \vartheta = \frac{\lambda^2}{3a^2} (h^2 + k^2 + hk) + \frac{\lambda^2}{4c^2} l^2 = \frac{a^{*2}}{4} \cdot s + \frac{c^{*2}}{4} l^2 \quad (1)$$

The result of this together with the unit cell dimensions derived from the coefficients to s and l^2 are given in Table 1 ($\lambda = 1.5418 \text{ \AA}$).

The number of molecules per hexagonal unit cell of Cs_4PbCl_6 is found from the unit cell volume, density of the crystals and molecular weight to be 5.9, i. e. 6. As it is beyond doubt that Cs_4PbBr_6 and Cs_4PbI_6 are both isomorphous with Cs_4PbCl_6 , it is concluded that they also have 6 molecules per hexagonal unit cell (or 2 molecules per rhombohedral unit cell).

⁴ W. FRANK, Unpublished work.

TABLE 1. Comparison of observed and calculated $\sin^2\theta$ -values for
 Cs_4PbCl_6 , Cs_4PbBr_6 and Cs_4PbI_6

Indices <i>hkl</i>	Cs_4PbCl_6			Cs_4PbBr_6			Cs_4PbI_6		
	Intensity estimated	$10^4 \cdot$ $\sin^2\theta_{\text{obs.}}$	$10^4 \cdot$ $\sin^2\theta_{\text{calc.}}$	Intensity estimated	$10^4 \cdot$ $\sin^2\theta_{\text{obs.}}$	$10^4 \cdot$ $\sin^2\theta_{\text{calc.}}$	Intensity estimated	$10^4 \cdot$ $\sin^2\theta_{\text{obs.}}$	$10^4 \cdot$ $\sin^2\theta_{\text{calc.}}$
$\bar{1}012$	m-s	0132	0132	m	0120	0121	m	0109	0109
$11\bar{2}0$	m-s	0137	0137	m(-w)	0126	0126	m-w	0113	0113
$11\bar{2}3$	s	0330	0330	m	0304	0304	vw?	027 ₀	0273
$21\bar{3}1$	(v)w	0341	0340
$\bar{2}\bar{1}32$	vw	0373	0373	(v)w	0335	0334
$10\bar{1}4$	w-m	0389	0388
$30\bar{3}0$	(v)s	0411	0410	(m)-s	0378	0378	m(-w)	0339	0338
$\bar{2}024$	m-s	0526	0525	m-s	0485	0485	m	0435	0434
$22\bar{4}0$	vw	0547	0547
$\bar{3}\bar{1}41$	m	0614	0614	m-s	0566	0566	m(-s)	0506	0506
3033	vw?	0496	0498
$21\bar{3}4$	(m)-s	0662	0662	s	0611	0611	m-s	0547	0547
$31\bar{4}2$	(w)-m	0679	0678	w-m	0626	0625	m	0560	0560
$22\bar{4}3$	(m)-s	0740	0740	s	0683	0682	(m)s	0610	0610
0006	w	0772	0772	w-m	0712	0713	w	0639	0639
$\bar{4}042$	vw	0815	0815
$\bar{2}\bar{1}35$	w	0856	0856	vw	0789	0789	vw	0706	0707
$32\bar{5}1$	vw?	0888	0888
$11\bar{2}6$	w-m	0909	0910	w-m	0838	0839
$\bar{3}\bar{1}44$	w-m	0936	0935	w	0862	0863	vw	0772	0772
$41\bar{5}0$	w-m	0957	0957	m-w	0882	0882	w	0788	0789
$40\bar{4}4$	w	1072	1072	vw	0989	0989	vw?	0885	0886
$31\bar{4}5$	w-(m)	1130	1128	w	1042	1041	w	0932	0932
$41\bar{5}3$	w-m	1150	1150	v-w	1061	1060
$30\bar{3}6$	w	1183	1182
$32\bar{5}4$	s-m	1209	1209	m-s	1116	1115	m	0996	0997
$33\bar{5}0$	m	1229	1230	w	1135	1134 _s	(v)w	1012	1013 _s
$\bar{4}261$	w	1298	1298
$22\bar{4}6$	w-m	1319	1320	w	1216	1217	w	1090	1089
$42\bar{6}2$	w	1362	1362
$\bar{1}018$	w	1419	1418	w	1310	1309	w	1173	1174
$51\bar{6}1$	w	1434	1434	(v)w	1323	1323	w	1179	1182
$\bar{5}054$	w	1481	1482	vw	1366	1367
$20\bar{2}8$	w	1556	1555	vw?	1433	1435	vw?	c. 1284	1286
$\bar{4}264$	w	1621	1619
$\bar{3}\bar{1}47$	w-m	1645	1644
6060	w	1512	1513	m-w	1353	1351
$\bar{2}\bar{1}38$	w	1692	1692	vw	1562	1561	vw	1399	1399
$41\bar{5}6$	w	1729	1730

(to be continued)

TABLE 1 (continued).

Indices <i>hkl</i>	Cs ₄ PbCl ₆			Cs ₄ PbBr ₆			Cs ₄ PbI ₆		
	Intensity estimated	10 ⁴ . sin ² θ _{obs.}	10 ⁴ . sin ² θ _{calc.}	Intensity estimated	10 ⁴ . sin ² θ _{obs.}	10 ⁴ . sin ² θ _{calc.}	Intensity estimated	10 ⁴ . sin ² θ _{obs.}	10 ⁴ . sin ² θ _{calc.}
51 $\bar{6}$ 4	v-w	1755	1756
52 $\bar{7}$ 0	w	1776	1777	vw	1638	1639	vw	1460	1464
43 $\bar{7}$ 2			1772						..
42 $\bar{6}$ 5	vw?	181 ₄	1812	s	1495	1494
11 $\bar{2}$ 9	(v)-w	1875	1875
5 $\bar{1}$ 65	vw	194 ₉	1950	vw	1796	1798	vw	160 ₆	1608
6 $\bar{1}$ 71	(v)-w	1985	1981	vw	163 ₁	1632
6 $\bar{1}$ 72	(v)-w	2044	2046	vw	1880	1886
43 $\bar{7}$ 4	v-w	2028	2029			
4048	vw	2102	2102
10 $\bar{1}$ 10	vw	2193	2192	vw?	181-	1813
5057			2190			1807
3 $\bar{2}$ 58	m	2241	2239	vw	2067	2065	vw	1848	1849
22 $\bar{4}$ 9	w	2283	2285	vw	2111	2108	vw?	1887	1888
61 $\bar{7}$ 5	m-s	2298	2302
5058	vw?	2318	2317	vw	2075	2072 ₅
5384	w-m	2122	2122 ₅
70 $\bar{7}$ 4			
Unit cell:	$a = 13.18_7 \text{ \AA}; c = 16.64_1 \text{ \AA}$ Vol: 2506 Å ³			$a = 13.73_2 \text{ \AA}; c = 17.32_4 \text{ \AA}$ Vol: 2829 Å ³			$a = 14.52_8 \text{ \AA}; c = 18.31_8 \text{ \AA}$ Vol: 3447 Å ³		

Volume increments

It would seem interesting to compare the molar volumes of the compounds Cs₄PbX₆ and CsPbX₃ obtained from X-ray analysis with the (crystal) molar volumes of CsX and PbX₂. The latter have been calculated from the molecular weights and the densities of the simple, crystalline compounds, but practically the same values are obtained from X-ray determination of the unit cell dimensions.⁵ Table 3 shows the result of this comparison. The "calculated" molar volumes are those to be expected from the molar volumes of CsX and PbX₂ if the rule about additivity of molar volumes were valid.

In all cases of formation of these compounds from simpler ones there is thus seen to be an increase in volume. It amounts to roughly 6 cc per

⁵ G. WAGNER u. L. LIPPERT. *Z. phys. Chem. B.* **31**, 263, (1936). R. W. G. WYCKOFF: *Crystal Structures* Vol. I Chapter IV. New York 1948.

TABLE 2. Molar volumes and volume increments per gr.-atom halogen

Compound	X = Cl	X = Br	X = J		
CsX	42.4 cc	48.0 cc	57.6 cc		
PbX ₃	47.6 -	55.0 -	74.8 -		
CsPbX ₃ {	Calculated	90.0 -	103.0 -	132.4 -	
	Observed	106.0 -	120.5 -	141.9 cc 134.1 cc (perovskite) (orthorh.)	
	Increment per X	5.3 -	5.8 -	3.2 cc 0.6 cc	
Cs ₄ PbX ₆ {	Calculated	217.2 -	247.0 -	305.2 cc	
	Observed	251.5 -	283.9 -	346.0 -	
	Increment per X	5.7 -	6.2 -	6.8 -	

gramatom of halogen except for CsPbI₃ in which it is practically negligible for the orthorhombic form.

As the structure of the latter compound—and also the structures of PbX₂—strongly indicate polarization of the halogen ions by the Pb-ions it seems reasonable to guess that the volume increments are connected with a change of the Pb-X-bonding—presumably an increase of ionic character—. In the perovskite-like structures of CsPbX₃ the less economic packing of the ions makes it possible for the caesium and the halogen ions to “choose” among several close-lying potential minima (1).

If this is the case also in crystals of the Cs₄PbX₆-compounds, one might expect difficulties in localizing the Cs- and X-atoms accurately by X-ray methods.

Atomic arrangements

With six molecules Cs₄PbCl₆ in a unit cell belonging to space group No. 167 most of the atomic positions should be fixed by symmetry and only four parameters have to be determined.⁶

Patterson projections on the plane ($\bar{1}2\bar{1}0$) were calculated for both Cs₄PbCl₆ and Cs₄PbBr₆ from Weissenberg diagrams taken about a twofold axis (crystal dimensions were about 75 μ). The results are shown in figs. 1 and 2. The maxima at $(0, \frac{1}{4})$ are required by space group No. 167 if 6 Cs' are placed in the special positions “a” and 6 Pb in the special positions “b” (see Ref. 6 p. 275). The remaining 18 Cs"-atoms are then likely to be in special positions “e”, and on this assumption the peaks marked Cs-Cs

⁶ International Tables for X-Ray Crystallography. Volume I. London 1952.

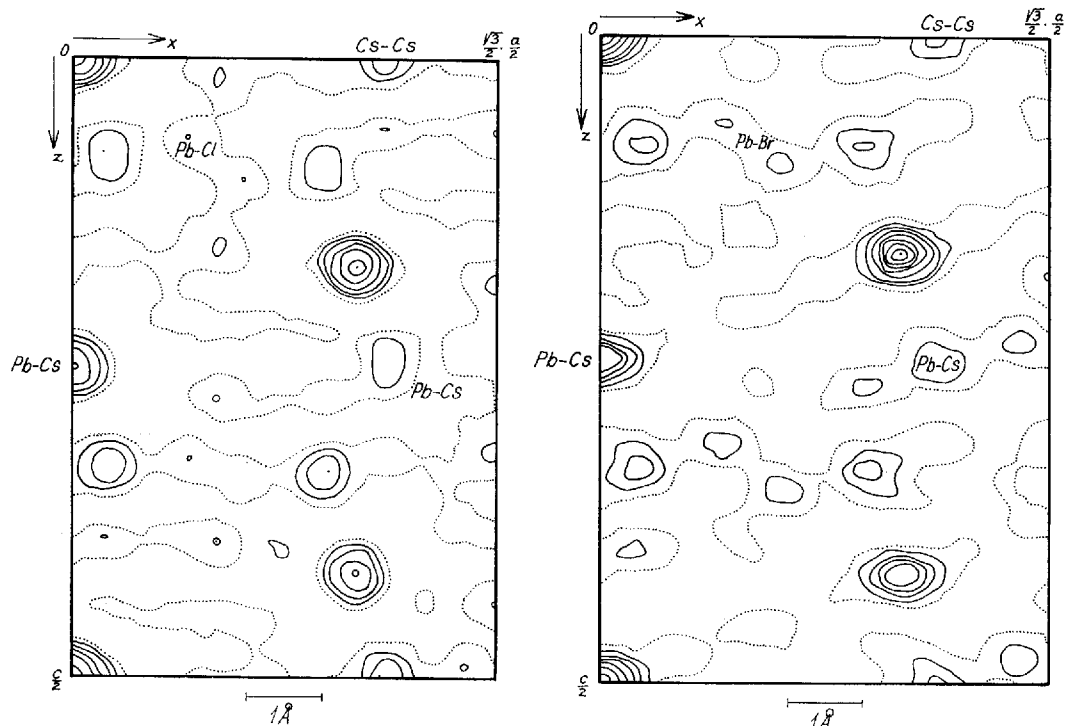


Fig. 1 and 2. Patterson projections on $(1\bar{2}10)$ of Cs_4PbCl_6 (left) and Cs_4PbBr_6 (right). Contour lines have been drawn at the (relative) levels: 0 (broken line) 50, 100, 150, 200, 300, 350.

and Pb-Cs provide the only missing Cs-parameter: $x = 0.37$. Having fixed the Pb- and Cs-atoms we are able to determine the signs for most of the structure factors $F(h0\bar{h}l)$ of Cs_4PbCl_6 , and an electron projection on $(1\bar{2}10)$ was calculated. This is fairly well resolved (fig. 3). It is possible to locate the Cl-atoms with some certainty and thus to determine the still remaining three Cl-parameters. Structure factors calculated from the atomic parameters obtained in this way and from atomic scattering factors corrected for dispersion effects (1) show a fair agreement with the observed ones. However, attempts to refine the structures either by trial and error or from difference synthesis of $\rho_{\text{obs.}} - \rho_{\text{calc.}}$ were not successful (even less so for Cs_4PbBr_6 !). The differences between strong and weak reflections obtained experimentally are much less pronounced than indicated by the calculated structure factors. This might be due to extinction, which is almost certain to be of importance in these crystals. Although no immediate absorption effects can be seen on the Weissenberg diagrams such ones may also be responsible for the lack of

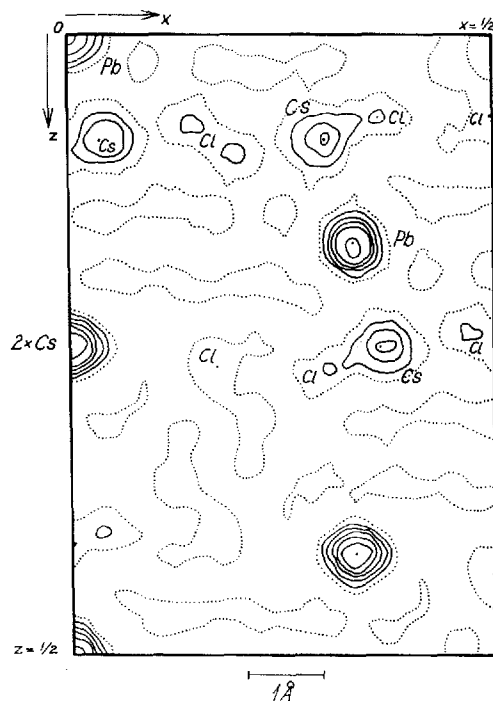


Fig. 3. Electron projection on $(1\bar{2}10)$ of Cs_4PbCl_6 . Contour lines have been drawn as in figs. 1 and 2.

agreement: The shape of the crystals did not even approximate to something having cylindrical symmetry. (It would have been desirable to use much smaller crystals, but it was found very difficult to mount them along a body diagonal without using a micromanipulator).

However, the difference syntheses indicate that a better agreement between observed and calculated structure factors presumably could be obtained by reducing the atomic scattering factors for the Cs'' -atoms in one way or another. This means formally introduction of a special, anisotropic temperature factor for these atoms, and physically a small delocalization of them around the average positions. In fact, it is possible in this way to get a somewhat better agreement in certain regions, but, as will be understood from the above, our measured intensities do not seem accurate enough and the whole procedure has been left out here. It is interesting that considerations of this kind achieved a definite improvement in the case of the perovskite-like structures of CsPbX_3 (1).

Although a completely satisfactory solution of the problem has not been

TABLE 3. Comparison of calculated and observed F-values for Cs_4PbCl_6

Indices <i>hkl</i>	$F_{\text{calc.}}$	$ F_{\text{obs.}} $	Indices <i>hkl</i>	$F_{\text{calc.}}$	$ F_{\text{obs.}} $	Indices <i>hkl</i>	$F_{\text{calc.}}$	$ F_{\text{obs.}} $
006	-180	118	70 $\bar{1}4$	19		211	24	
0012	220	182	70 $\bar{8}$	80	112	214	102	104
0018	-80	115	70 $\bar{2}$	17	54	217	-11	
10 $\bar{2}0$	74	108	704	88	65	2110	29	
10 $\bar{1}4$	12		7010	22		2113	4	
10 $\bar{8}$	91	87	7016	52		2116	60	79
10 $\bar{2}$	58	65	80 $\bar{1}6$	164	126	2119	-1	
104	66	52	80 $\bar{1}0$	-72	71	312	78	83
1010	64	71	80 $\bar{4}$	170	160	315	-66	58
1016	35		802	-51	60	318	43	52
20 $\bar{1}6$	104	180	808	126	123	3111	42	
20 $\bar{1}0$	-16		8014	-25		3114	58	
20 $\bar{4}$	147	125	90 $\bar{1}2$	39		3117	-26	
202	-2		90 $\bar{6}$	42	65	3120	27	52
208	117	121	900	63	72	410	82	86
2014	3		906	18		413	61	52
2020	75	97	9012	78	86	416	44	45
30 $\bar{1}8$	-36		100 $\bar{1}4$	10		419	-41	
30 $\bar{1}2$	142	166	100 $\bar{8}$	74	93	4112	55	63
30 $\bar{6}$	-53	58	100 $\bar{2}$	7		4115	29	
300	208	132	1004	86	108	4118	37	
306	-79	71	10010	2		511	79	70
3012	172	186	110 $\bar{1}0$	-76		514	73	63
3018	-70	46	110 $\bar{4}$	172	123	517	-64	43
40 $\bar{2}0$	48	76	1102	-91		5110	38	
40 $\bar{1}4$	28		1108	166	134	5113	44	
40 $\bar{8}$	74	97	120 $\bar{1}2$	36		5116	50	58
40 $\bar{2}$	46	67	120 $\bar{6}$	46		5119	-28	
404	72	82	1200	31	39	612	50	81
4010	53	44	1206	50		615	-97	88
4016	35		12012	28		618	41	54
50 $\bar{1}6$	104	110				6111	85	88
50 $\bar{1}0$	-28					6114	48	
504	163	152	012	58	36	710	52	58
502	-58	80	018	92	86	713	15	
508	169	152	0114	11		716	40	
5014	-63	60	0120	73	86	719	-12	
5020	134	97	110	54	63	7112	61	50
60 $\bar{1}8$	-26		113	90	65	7115	10	
60 $\bar{1}2$	129	125	116	82	71	811	28	
60 $\bar{6}$	-54	50	119	-80	65	814	72	81
600	179	177	1112	37		817	-26	
606	-54	50	1115	66	63	8110	30	
6012	130	126	1118	51		8113	24	
6018	-28		1121	-61	52	8116	41	56

TABLE 4. Comparison of calculated and observed F-values for Cs_4PbBr_6

Indices <i>hkl</i>	F _{calc.}	F _{obs.}	Indices <i>hkl</i>	F _{calc.}	F _{obs.}	Indices <i>hkl</i>	F _{calc.}	F _{obs.}
006	-251	126	40 $\bar{1}4$	11		80 $\bar{1}6$	219	184
0012	246	210	40 $\bar{8}$	97	117	80 $\bar{1}0$	-120	93
0018	-52		40 $\bar{2}$	37	42	80 $\bar{4}$	172	153
10 $\bar{2}0$	106	130	404	62	82	802	-10	
10 $\bar{1}4$	-22	33	4010	77	81	808	72	61
10 $\bar{8}$	113	88	4016	12	20	8014	16	
10 $\bar{2}$	70	81	50 $\bar{1}6$	79	92	90 $\bar{1}2$	10	
104	22		50 $\bar{1}0$	20	32	90 $\bar{6}$	76	100
1010	109	122	50 $\bar{4}$	118	139	900	47	
1016	10	42	502	-46	55	906	36	19
1022	46	46	508	200	178	9012	101	94
20 $\bar{1}6$	126	161	5014	-49	83	100 $\bar{1}4$	4	
20 $\bar{1}0$	-37	30	5020	201	169	100 $\bar{8}$	76	93
20 $\bar{4}$	154	158	60 $\bar{1}8$	-9	20	100 $\bar{2}$	12	
202	10		60 $\bar{1}2$	129	127	1004	85	78
208	98	176	60 $\bar{6}$	-72	90	10010	-1	
2014	17		600	214	189	110 $\bar{1}0$	-63	
2020	73	101	606	-72	59	110 $\bar{4}$	172	107
30 $\bar{1}8$	-25		6012	140	116	1102	-98	36
30 $\bar{1}2$	110	111	6018	25		1108	174	101
30 $\bar{6}$	-9	19	70 $\bar{1}4$	-2		11014	-74	
300	179	188	70 $\bar{8}$	115	118	120 $\bar{1}2$	17	49
306	-78	55	70 $\bar{2}$	-73		120 $\bar{6}$	70	
3012	197	251	704	127	85	1200	15	24
3018	-98	72	7010	12	39	1206	54	35
40 $\bar{2}0$	59	69	7016	61	33	12012	42	14

obtained, it seems unlikely that the atomic positions can be very wrong. They are listed in Table 5 and interatomic distances calculated on the basis of this in Table 6. The latter compare quite reasonably with values obtained from the structures of CsPbCl_3 and CsPbBr_3 , and, as there, the Pb-atoms are surrounded by 6 halogen atoms, which form a nearly regular octahedron (symmetry: $4\bar{3}m$). In the present structures the octahedron is compressed along a trigonal axis—viz. the one parallel to the c-axis of the crystals—so that the symmetry becomes $\bar{3}m$ only. The XPbX-angle, where the two X-atoms have the same z-coordinate, is also given in Table 6.

From what has been said above, it is clear that these results must be taken with a certain reservation, and the uncertainty as to the obtained interatomic distances may easily be 0.10 Å, thus making the deviation of these angles from 90° illusory.

Six X-atoms belonging to two different PbX_6 -octahedra form trigonal prisms (symmetry $32m$) with the Cs'-atoms as centres, the Cs'-X distances

TABLE 5. Atomic positions in Cs_4PbX_6

	$(0, 0, 0);$	$\left(\frac{1}{3}, \frac{2}{3}, \frac{2}{3}\right);$	$\left(\frac{2}{3}, \frac{1}{3}, \frac{1}{3}\right) +$
6 Pb in $\bar{3}$:	$(0, 0, 0);$	$\left(0, 0, \frac{1}{2}\right)$	
6 Cs' in 32:	$\left(0, 0, \frac{1}{4}\right);$	$\left(0, 0, \frac{3}{4}\right)$	
18 Cs'' in 2:	$\left(x, 0, \frac{1}{4}\right);$	$\left(0, x, \frac{1}{4}\right);$	$\left(\bar{x}, \bar{x}, \frac{1}{4}\right); \left(\bar{x}, 0, \frac{3}{4}\right); \left(0, \bar{x}, \frac{3}{4}\right); \left(x, x, \frac{3}{4}\right)$
	For Cs_4PbCl_6 $x = 0.370$ and for Cs_4PbBr_6 $x = 0.372$		
36 X in 1:	$(x, y, z);$	$(\bar{y}, x-y, z);$	$(y-x, \bar{x}, z); \left(\bar{y}, \bar{x}, \frac{1}{2} + z\right); \left(x, x-y, \frac{1}{2} + z\right); \left(y-x, y, \frac{1}{2} + z\right);$ + inverse positions.
	For Cl in Cs_4PbCl_6 : $x = 0.040$ $y = 0.164$ $z = 0.095$		
	For Br in Cs_4PbBr_6 : $x = 0.035$ $y = 0.170$ $z = 0.099$		

TABLE 6. Interatomic distances between nearest neighbours in Cs_4PbX_6

Distance (frequency)	From this study	From PAULING's ionic radii	From GOLDSCHMIDT's ionic radii	From CsPbX_3 in Ref. 1.
Pb-Cl (6)	2.93 Å	3.02 Å	3.13 Å	2.86 Å
Cs'-Cl (6)	3.57 -	3.50 -	3.48 -	(3.68)-
Cs''-Cl (2)	3.59 -			
Cs''-Cl (2)	3.85 -			
Cs''-Cl (2)	3.43 -			
Cs''-Cl (2)	3.43 -			
Cl-Cl	4.01-4.28 Å			
\sphericalangle ClPbCl	93.6°			
Pb-Br (6)	3.12 Å	3.16 Å	3.28 Å	2.99 Å
Cs'-Br (6)	3.69 -	3.64 -	3.63 -	(3.85)-
Cs''-Br (2)	3.67 -			
Cs''-Br (2)	3.93 -			
Cs''-Br (2)	3.65 -			
Cs''-Br (2)	3.60 -			
Br-Br	4.31-4.52 Å			
\sphericalangle BrPbBr	92.8°			

not being very different from the values expected from ionic radii.⁷—The remaining 18 Cs''-atoms in positions of rather low symmetry are each

⁷ LANDOLT-BÖRNSTEIN. I. Band, 4. Teil, p. 523. Springer Verlag 1955.

surrounded by 8 X-atoms, 2×3 from two PbX_6 -octahedra and 2×1 from two others, but here the Cs"-X-distances vary considerably, and it is conceivable that a disordered structure may result.

The crystals of Cs_4PbX_6 thus contain isolated PbX_6 -----octahedra linked together by the positive Cs^+ -ions.

Discussion

Apart from the supposition about disorder our conclusions concerning the structures of the Cs_4PbX_6 -compounds are in complete agreement with the findings of G. BERGERHOF and O. SCHMITZ-DUMONT in the isomorphous K_4CdCl_6 -crystals. This again illustrates the similarity between divalent Pb^{++} and Cd^{++} previously demonstrated in the case of the CsPbI_3 and MeCdCl_3 compounds.⁸ It is interesting that the compounds Cs_4PbX_6 with isolated PbX_6 -octahedra are precipitated from concentrated solutions of CsX , whereas from less concentrated solutions crystals are obtained in which such octahedra share X-atoms, e. g. in the perovskite-like structures of CsPbX_3 , or in the one-dimensional polynuclear complex ion $(\text{PbI}_3^-)_n$ in CsPbI_3 (8). It thus seems likely that the concentrated solutions mainly contain isolated highly symmetrical PbX_6 -----ions, while in less concentrated ones bi-, tri- — — or polynuclear complex ions built up from such units may be prevailing. This may add to our understanding of the problem why in concentrated salt solutions the behaviour of some electrolytes approaches to that of electrolytes in extremely dilute solutions.

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⁸ C. K. MØLLER. The Structure of CsPbI_3 , Mat. Fys. Medd. Dan. Vid. Selsk. **32**, No. 1 (1959).

