THE STRUCTURE OF CÆSIUM PLUMBO IODIDE CsPbI₃

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Synopsis

$CsPbI_3$ is obtained from aqueous solutions as yellow, orthorhombic crystals belonging to space group No. 62 Pmnb. The unit cell contains 4 molecules, and $a = 4.797$ Å, $b = 10.46_2$ Å, $c = 17.78_8$ Å. Heated to 305—308° C. these crystals are transformed into a black modification which has a monoclinically distorted perovskite-like structure: $a = b = 6.15_2$ Å, $c = 6.22_8$ Å, $\beta = 88°.1_5$. X-ray analysis by Fourier methods of the yellow crystals shows that distorted PbI_6-octahedra sharing I-atoms form one-dimensional, polynuclear complex ions, $(PbI_3^-)_n$, running parallel to the a-axis. The Pb-I distances vary from 3.01 Å to 3.42 Å. Nine I-atoms belonging to three different complex ions of this type are nearly di-tri-gonally arranged around each Cs-atom, with CsI-distances 3.87—4.19 Å. This structure is analogous to that of M^1CdCl_3.

Introduction

Divalent lead is known to form complex ions with the halogen ions which together with alkali metal ions give compounds of the general compositions[1, 2]

$$M_4^I PbX_6, \quad M^I PbX_3, \quad and \quad M^I Pb_2 X_5.$$

Some of these compounds crystallize with crystal water—apparently the size of the alkali metal ion is of importance in this connection—but the Cs-salts, as far as they are known, form crystals which do not contain water.

From an interest in the stereochemistry of divalent lead in simple compounds it was decided to investigate some of these crystals, as, with spherical anions all of the same kind and no water in the lattice, one might hope to discover the "intrinsic" symmetry of the Pb^{++}-ion and also obtain reliable interatomic distances.

It is true that the PbX_2-compounds have been investigated long ago,[3] but only $PbBr_2$ and $PbCl_2$ are similarly built, and they have rather unusual structures, from which it seems difficult to extract information about the symmetry of the electronic arrangement in the Pb^{++}-ion in general. Also compounds of the type MPb_2X_5 have been investigated by POWELL and TASKER[4] and will not be discussed here; suffice it to say that these authors find that in crystals of $RbPb_2Br_5$ there are chains of Rb^+ and Br^--ions, whereas the Pb-atoms tend to form molecules $PbBr_2$ with interatomic distances $r_{Pb-Br} = 2.89 \pm 0.04$ Å.

In this paper the structure of $CsPbI_3$ will be described. The structures of $CsPbCl_3$, $CsPbBr_3$, and Cs_4PbCl_6 will be dealt with in later publications.

[1] N. V. SIDGWICK, *Chemical elements and their compounds*. Vol. I p. 626. Oxford Univ. Press.
[2] GMELIN-KRAUT, *Handbuch d. anorg. Chemie*. IV. Band, 2. Teil, pp. 358, 376, 551, 555.
[3] See e. g. R. W. G. WYCKOFF, *Crystal Structures*. Volume I. Interscience Publishers, New York 1948, where references can be found. See also A. F. WELLS, *Structural inorganic chemistry*. Oxford 1945. Chapters 8 and 16.
[4] H. M. POWELL and H. S. TASKER, *J. Chem. Soc.* London 1937, p. 113.

Preparation

According to H. L. WELLS and coworkers[5] yellow crystals of composition $CsPbI_3$ can be obtained by dissolving PbI_2 in a hot aqueous solution of CsI and then leaving it to cool. As PbI_2 is only slightly soluble in a CsI solution only poor yields can be obtained in this way. Accidentally it was found that yellow crystals with composition $CsPbI_3$ can be obtained by the following procedure: $PbBr_2$ is dissolved in a hot, rather concentrated solution of CsBr and CsI (in about equal amounts, but apparently this is not important). On addition of water to this solution small yellow needle- or lath-shaped crystals precipitate. Qualitative tests on these crystals for Cs, Pb, and I were all positive. Instead of making a quantitative analysis the composition has been ascertained in the following way. Equimolar quantities of very pure CsI and PbI_2 after weighing have been fused in a crucible and cooled. The black reaction product changes to a yellow substance during some hours without change in weight, and the latter gives the same X-ray powder diagram as that obtained from powders of the yellow crystals precipitated in aqueous solution.

Properties and polymorphism

The yellow $CsPbI_3$ crystals are very slowly decomposed by water under precipitation of PbI_2. Under the polarizing microscope they show birefringence and parallel extinction. When heated on a hot stage under the microscope they can be seen to undergo a phase change at 305—308° C.: the crystals become black and lose their transparency. When the product is left to cooling again the yellow crystals reappear, but only slowly, and in fact it has been possible to undercool the black substance to room temperature for several days before the yellow crystals appeared again.

When equimolar quantities of CsI and PbI_2 are fused together a deep purple liquid is obtained which solidifies to a black graphite-like mass. Left to itself in the open air this black substance changes to the yellow form of $CsPbI_3$, and no change in weight can be observed. When kept in a desiccator the black form can sometimes be preserved for several months so that it looks as if the humidity in the air has a catalytic effect on the transformation. If the black form is heated to temperatures a little above 310° C. it gradually changes to another yellow product, which has a different crystal structure, but it has not been further investigated.

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

X-ray examination. Unit cell dimensions

X-ray powder diagrams of crushed yellow $CsPbI_3$-crystals obtained from aqueous solutions and the low temperature yellow conversion product of black $CsPbI_3$ from the melt were taken in a Guinier type focusing camera with monochromatic CuK_α-radiation and were found to be identical within the accuracy of our measurements. In order to obtain accurate $\sin^2\vartheta$-values powdered NaCl was added to the powder specimen and a calibration curve was drawn each time from which corrections to the measured $\sin^2\vartheta$-values could be obtained (Table 1). As the black form of $CsPbI_3$ is not very stable its X-ray powder diagram was obtained on a GE XRD-3 diffractometer. The substance was melted on a stainless steel holder, brought into position

TABLE 1. Observed and calculated $\sin^2\vartheta$-values for yellow $CsPbI_3$. CuK_α-radiation

Indices	Estimated intensity	$10^4 \cdot \sin^2\vartheta$ obs.	$10^4 \cdot \sin^2\vartheta$ calc.	Indices	Estimated intensity	$10^4 \cdot \sin^2\vartheta$ obs.	$10^4 \cdot \sin^2\vartheta$ calc.
011	m	0072	0073	042	vw?	0943	0944.5
002	m	0075	0075	125			0944
012	m-s	0129	0129	035	vw; diff.	0959	0958
020	vw?	0217	0217	116	w	0988	0988
013	vw	0223	0223	200	m; diff.	1031	1033
021	w	0236	0236	134	m	1045	1047
022	vw?	0293	0292	027	vw	1137	1137
111	s-m	0332	0331	142	w-m	1202	1202
014	m	0355	0355	008			
023	m-s	0387	0386	117	m-s	1232	1232
120	w	0475	0475	143	w	1296	1296
113	m-s	0481	0481	037	vw; diff.	1412	1409
121	s	0494	0494	052	vw	1432	1433
024	w-m	0518	0518	118	vw?	1513	1514
015	m	0524	0524	215	w-m, br	1553	1551
122	vs	0550	0550	224			1556
123	vw	0644	0644	232	vw	1596	1597
105	m-s, diff.	0728	0727.5	145			1596.5
016			0730	216	vw	1760	1763
131	vw	0765	0766	154	vw, br, diff.	1918	1916
034	(v)w	0789	0789	241			1921
132	m	0821	0822	048	w	2068	2071
133	vw	0915	0916	313	vw, br, diff	2550	2548
				322	vw, br, diff	2616	2615

br = broad, diff = diffuse, m = medium, s = strong, v = very, w = weak.

while still hot ($\sim 200°$ C.), and during the following hours several runs were made of the powder diagram of the same sample. Immediately after mounting, the specimen gave a very simple diagram, but this gradually changed and finally—usually after two hours—a diagram characteristic of the yellow $CsPbI_3$ was obtained. Simultaneously the colour of the specimen had changed from black to dirty yellow. From the accurate $\sin^2 \vartheta$-values

TABLE 2. Observed and calculated $\sin^2 \vartheta$-values for black
$CsPbI_3$. CuK_{α}-radiation

Indices	Estimated intensity	$10^4 \cdot$ $\sin^2 \vartheta$ obs.	$10^4 \cdot$ $\sin^2 \vartheta$ calc.	Indices	Estimated intensity	$10^4 \cdot$ $\sin^2 \vartheta$ obs.	$10^4 \cdot$ $\sin^2 \vartheta$ calc.
001	} s	0164	{ 0153	102	} vw	0791	{ 0785
100			{ 0157	210			{ 0790
101			{ 0300	112	vw	0912	0907
011	w-m	0307	{ 0310	$11\bar{2}$	} vw	0948	0947
110			{ 0314	121			
$10\bar{1}$	(v)w	0327	0320	202	w-m	1206	1201
$\frac{1}{2}\frac{3}{2}\frac{1}{2}$	(v)w	0438	0431	022	w-m	1234	1241
111	w-m	0454	0457	$20\bar{2}$	w	1285	1281
$11\bar{1}$	w-m	0475	0477	212	w	1362	1358
$\frac{1}{2}\frac{3}{2}1$	(v)w	0548	0546	222	w-m	1816	1829
002	s	0613	0613	$22\bar{2}$	w	1899	1909
020	vs	0628	0628	004	vw	2445	2451
$\frac{3}{2}\frac{3}{2}0$	vw	0714	0707	400	vw	2515	2512

obtained for the yellow $CsPbI_3$ in the Guinier camera a calibration was made for the diffractometer readings and so $\sin^2 \vartheta$-values could be determined for the black variety, too. However, the accuracy of the latter $\sin^2 \vartheta$-values is not high as the scanning had to be fast (Table 2).

Oscillation and Weissenberg diagrams were also taken of single crystals of the yellow $CsPbI_3$ and orthorhombic symmetry was established for these crystals. Preliminary values of the axes were determined from these photographs (camera diameter: 57.3 mm), and were used as basis of a first indexing of the powder photographs. By trial and error refined values were finally obtained from the quadratic form:

$$\sin^2 \vartheta = 0.02583 \, h^2 + 0.005430 \, k^2 + 0.001878 \, l^2, \qquad (1)$$

which gave satisfactory agreement between observed and calculated $\sin^2 \vartheta$-values (Table 1).

The unit-cell dimensions derived from the coefficients in (1) are with $\lambda(CuK_\alpha) = 1.5418$ Å:

$$a = 4.797 \pm 0.005 \text{ Å}; \quad b = 10.46_2 \pm 0.01 \text{ Å}; \quad c = 17.78_8 \pm 0.02 \text{ Å}.$$

Unit-cell volume: $892._3$ Å^3. Molar volume of unit cell: $892._3 \, 10^{-24} \cdot 6.0228 \cdot 10^{23}$ $= 537.4$ cm^3.

The strongest lines on the powder diagram of the black $CsPbI_3$ indicated a tetragonal lattice with cell dimensions $a = 6.15$ Å, $c = 6.23$ Å. But in order to account for the observed splittings of the weaker lines, it proved necessary to use a monoclinic quadratic form:

$$\sin^2 \vartheta = 0.01570 \, (h^2 + k^2) + 0.01532 \, l^2 - 0.0010 \, h \, l \qquad (2)$$

corresponding to a unit cell with dimensions:

$$a = b = 6.15_2 \pm 0.03 \text{ Å}; \quad c = 6.22_8 \pm 0.03 \text{ Å}; \quad \beta = 88°.15 \pm 0°.5.$$

Unit-cell volume: $235._6$ Å^3. Molar volume of unit cell: $235._6 \cdot 10^{-24} \cdot 6.0228 \cdot 10^{23}$ $= 141._9$ cm^3.

Even so a few (very) weak lines still persisted and it seems only possible to include them in the above indexing by assuming a doubling of the cell dimensions. A similar doubling has also been found in the perovskite-like crystals of $CsPbBr_3$ and can there be explained in terms of a superstructure.[6] It seems reasonable that the same explanation applies to $CsPbI_3$ as well.

For convenience the black form of $CsPbI_3$ will be referred to the small monoclinic unit cell with the dimensions given above—although this monoclinic indexing is not quite without ambiguities, mainly due to inaccurate data. The weak lines, which require a doubling of cell dimensions, therefore appear with fractional indices in Table 2.

The molar volumes of CsI and PbI_2 calculated from the molecular weights and the density of the crystals of CsI and PbI_2 are 57.6 cm^3 and 74.8 cm^3, respectively. Assuming additivity of molar volumes, we should expect a crystal molar volume 132.4 cm^3 for $CsPbI_3$ or on an average a volume $132.4 \div 6.0228 \cdot 10^{23} = 219._8$ Å^3 per single molecule of $CsPbI_3$. From this we infer that the yellow $CsPbI_3$ has four molecules in the unit

[6] C. K. Møller, Nature 182, 1436 (1958).

cell, whereas the black variety has only one in the small unit cell referred to above.

The black $CsPbI_3$ thus appears to have a monoclinically distorted perovskite structure and the intensity distribution on the powder diagram lends further support to this statement. As the general features of this type of structure will be discussed in another paper this modification will not be further considered here.

Space group of the yellow $CsPbI_3$

Weissenberg diagrams were taken of a single crystal of yellow $CsPbI_3$, 45 μ thick, of nearly circular cross section, length 0.10 mm. Visually estimated intensities were obtained by a multiple film technique and by using an intensity scale, prepared by taken a series of photographs of a strong reflection with increasing exposure times. When taking diagrams for intensity measurements, care was taken to keep film material, temperature, developer, fixer, X-ray intensity, and speed of the Weissenberg goniometer as constant as possible. The absorption has been neglected, or rather, it has been included in the isotropic part of the temperature factor, as it turns out that these two factors nearly cancel for the zeroth layer line.[7] Otherwise the usual corrections for polarization and Lorentz-factors have been applied[8] and approximate relative $|F(hkl)|^2$-values thus obtained. With the orthorhombic unit cell given above it was found that reflections of the type h0l were only present for $h+l$ even and similarly hk0 only for k even, whereas 0kl and hkl in general were not subjected to any systematic restrictions. These conditions are characteristic of space group No. 62 Pmnb and No. 33 $P2_1nb$.[9]

Furthermore, alternating layer lines taken about the a-axis were found to be identical, showing that $|F(h+2n, k, l)| = |F(hkl)|$, where n is an integer. This shows that the scattering matter must lie in planes separated by the distance $\frac{a}{2}$. The space group No. 62, with 4 molecules per unit cell and with the atoms in special positions, does in fact require intensity relations of the type observed, whereas No. 33 does not. Hence there is strong evidence for space group No. 62 with all the atoms in special positions a, b, or c.

[7] Compare C. W. Bunn, *Chemical Crystallography*, p. 207. Oxford Univ. Press 1946.
[8] W. Cochran, *J. Sci. Instr.* **25**, No. 7 (1948).
[9] *Internat. Tables for X-Ray Cryst.* I. London 1952.

Patterson and electron projections

A Patterson projection on the bc-plane was next calculated on a Hägg-Laurent Fourier machine[10] from the observed $|F(hkl)|^2$. The appearance of this projection showed that the special positions designated a and b in Ref. 9, p. 151, under space group No. 62 could be ruled out, as these po-

Fig. 1. Patterson projection of yellow $CsPbI_3$ on the bc-plane. Contour lines are drawn at the relative densities 0, 40, 60, 80, 100, 125, 150, 200, 600, 800.

sitions require high vector densities on the projection in places where either no such peaks appear or only rather small peaks show up. (Fig. 1).

We are thus left with the special positions c:

$$\left(\frac{1}{4}, y, z\right); \quad \left(\frac{3}{4}, \bar{y}, \bar{z}\right), \quad \left(\frac{3}{4}, \frac{1}{2}-y, \frac{1}{2}+z\right), \quad \left(\frac{1}{4}, \frac{1}{2}+y, \frac{1}{2}-z\right) \tag{3}$$

for the $5\cdot4$ atoms. It can easily be seen that e.g. four Pb-atoms in these positions give rise to vector peaks on the Patterson projection on the bc-plane in

[10] V. Frank, *J. Sci. Instr.* **34**, 210 (1957).

$$\left(0, \frac{1}{2}, \frac{1}{2} \pm 2z\right) \quad \left(0, \frac{1}{2} \pm 2y, \frac{1}{2}\right) \quad (0, 2y, \pm 2z). \tag{4}$$

Therefore the three strongest peaks on the Patterson projection which fulfil the relations expressed in (4), having been found, they were identified as Pb-Pb-maxima and the parameters y and z for the Pb-atoms could be determined straightforwardly, $(x, y, z) = \left(\pm\frac{1}{4}, 0.163, 0.059\right)$.

As the structure has a centre of symmetry in O, the structure factors all have phase angles 0 or π so that $F(hkl) = \pm |F(hkl)|$. We must determine these signs before a calculation of an electron projection can be undertaken. Hence the following considerations.

The highest measured $|F|$-value is that of 039. With the Pb-parameters obtained above the contribution from Pb to this structure factor is found to be nearly maximum and positive. If we assume that all the atoms in the unit cell give nearly maximum positive contributions to this structure factor a rough estimate shows that all the structure factors not less than half of F (039) must have the same sign as the Pb-contribution alone, provided that the latter is appreciable. In this way signs were unambiguously determined for 16 structure factors. An electron projection calculated on the basis of these sixteen structure factors together with the Patterson projection gave the parameters of two I-atoms, and then signs could be obtained for 46 structure factors by a reasoning similar to that above. A second electron projection with these terms next revealed all the atoms so that all the parameters could now be determined and structure factors calculated. With signs obtained from this last calculation all the experimentally determined structure factors were finally used in a third calculation of the electron projection on the yz-plane (fig. 2).

New structure factors calculated from atomic scattering factors corrected for dispersion effects[11] and the atomic parameters from this last projection were brought on an absolute scale by plotting $\log_{10}\left|\dfrac{F_{obs.}}{F_{calc.}}\right|$ versus $\sin^2\vartheta$. As, theoretically,[12] $F(\vartheta)_{obs.} = A \cdot F(\vartheta)_{calc.} \cdot \exp(-B\sin^2\vartheta)$ this plotting should approximately give a straight line with slope -B and intersect the ordinate

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[11] Atomic scattering factors were taken from W. H. BRAGG and W. L. BRAGG, *The Crystalline State* Vol. I, pp. 330—333 (London 1949), and corrections for dispersion effects from C. H. DAUBEN and D. H. TEMPLETON, *Acta Cryst.* 8, 841 (1955). See also R. W. JAMES, *Optical Principles of X-Rays*, p. 608 (London 1948).

[12] H. LIPSON and W. COCHRAN, *Determination of Crystal Structures*, p. 61. London 1953.

Fig. 2. Electron projection of yellow CsPbI₃ on the *bc*-plane. Contour lines are drawn at the relative electron densities 0, 100, 200, 300, 400, 500, and 600.

axis in $\log A$, thus providing the conversion factor $\dfrac{1}{A}$. (It has then been assumed that the effect of absorption can be included in the exponential term, the "temperature factor".[13] For the zeroth layer line we find in this way $B \simeq 0$).

Having brought observed and calculated F's on the same absolute scale corresponding to $F(000) = 288.8$, a difference synthesis was calculated from $F(0\,kl)_{\text{obs.}} - F(0\,kl)_{\text{calc.}}$ and corrections to the atomic parameters obtained from

$$\varDelta r = \left\{ \frac{\partial\,(\varrho_{\text{obs.}} - \varrho_{\text{calc.}})}{\partial\,r} \right\}_{r=r_0} \Bigg/ \left\{ \frac{\partial^2\,\varrho_{\text{obs.}}}{\partial\,r^2} \right\}_{r=r_0},$$

[13] Ref. 7. See also B. Jerslev, *Studier over Oximernes Struktur*, p. 25—26. Dissertation, Copenhagen 1958.

where approximate values for the denominators were estimated from the last electron projection ($\varrho_{obs.}$) and for the numerators from the difference projection ($\varrho_{obs.} - \varrho_{calc.}$). After these corrections had been applied to the atomic parameters, a definite improvement in the agreement between observed and calculated structure factors was obtained. (For the observed F-values R decreased from 0.17 to 0.11). Further refinement was not attempted, as we did not consider our measured intensities accurate enough for this purpose.

In order to ascertain the x-parameters $\left(\pm \dfrac{1}{4} \right)$ the structure factors for the first layer line were also measured and calculated. Although a reasonably good agreement is obtained also in this case, it is not quite so good as for the zero-th layer line—presumably due to the neglect of absorption, which is more serious for the non-zero layer lines. (Table 3).

TABLE 3. Comparison of calculated and observed structure factors for yellow $CsPbI_3$

(brought on an absolute scale corresponding to $F(000) = 289$)

Indices		0. layer line h = 0		1. layer line h = 1		Indices		0. layer line h = 0		1. layer line h = 1	
k	l	$F_{calc.}$	$|F_{obs.}|$	$F_{calc.}$	$|F_{obs.}|$	k	l	$F_{calc.}$	$|F_{obs.}|$	$F_{calc.}$	$|F_{obs.}|$
2	0	$\overline{22}$	27	54	40	1	5	$\overline{118}$	97	$\overline{12}$	
4	0	$\overline{49}$	39	$\overline{52}$	45	1	6	85	73	53	43
6	0	77	83	$\overline{22}$		1	7	$\overline{39}$	42	$\overline{111}$	128
8	0	$\overline{64}$	58	154	135	1	8	$\overline{46}$	51	55	53
10	0	$\overline{24}$	25	3		1	9	13		$\overline{59}$	58
12	0	46	35	$\overline{13}$		1	10	0		$\overline{86}$	85
0	2	37	28			1	11	$\overline{53}$	53	$\overline{49}$	53
0	4	20	16			1	12	$\overline{66}$	83	$\overline{39}$	60
0	6	21	18			1	13	$\overline{43}$	50	$\overline{19}$	
0	8	$\overline{33}$	37			1	14	$\overline{47}$	44	10	
0	10	43	35			1	15	18	35	10	
0	12	8				1	16	35	35	$\overline{9}$	
0	14	39	51			1	17	17	25	16	
0	16	64	64			1	18	$\overline{12}$		26	
0	18	115	120			1	19	3		19	
0	20	3				1	20	47	48	$\overline{4}$	
1	1	23	27	39	28	1	21			$\overline{64}$	70
1	2	37	32	6		2	1	22	23	$\overline{98}$	133
1	3	15	15	$\overline{73}$	60	2	2	$\overline{17}$	20	131	110
1	4	40	39	$\overline{4}$		2	3	60	57	$\overline{33}$	28

(To be continued)

TABLE 3 (continued)

Indices		0. layer line h = 0		1. layer line h = 1		Indices		0. layer line h = 0		1. layer line h = 1	
k	l	$F_{calc.}$	$\|F_{obs.}\|$	$F_{calc.}$	$\|F_{obs.}\|$	k	l	$F_{calc.}$	$\|F_{obs.}\|$	$F_{calc.}$	$\|F_{obs.}\|$
2	4	$\overline{93}$	87	25	18	4	2	$\overline{52}$	48	$\overline{75}$	75
2	5	26	23	$\overline{5}$		4	3	$\overline{105}$	99	$\overline{70}$	65
2	6	12		$\overline{37}$	35	4	4	$\overline{38}$	39	23	28
2	7	74	74	$\overline{3}$		4	5	$\overline{50}$	50	$\overline{31}$	23
2	8	38	41	26	18	4	6	$\overline{29}$	30	$\overline{45}$	50
2	9	$\overline{17}$		27	20	4	7	44	43	29	33
2	10	$\overline{3}$		$\overline{5}$		4	8	41	55	48	55
2	11	$\overline{113}$	102	$\overline{24}$	30	4	9	$\overline{20}$		$\overline{6}$	
2	12	9		11		4	10	30	34	48	43
2	13	6		25		4	11	21		$\overline{4}$	
2	14	$\overline{91}$	101	52	68	4	12	$\overline{59}$	67	$\overline{92}$	90
2	15	$\overline{41}$	35	21		4	13	31		25	35
2	16	$\overline{4}$		80	85	4	14	$\overline{33}$	39	$\overline{15}$	25
2	17	13		21		4	15	$\overline{43}$	48	34	35
2	18	4		38	40	4	16	$\overline{41}$	43	$\overline{65}$	73
2	19	49	53	53	60	4	17	$\overline{31}$	34	$\overline{15}$	
2	20	$\overline{34}$	37	41	28	4	18	$\overline{24}$	23	$\overline{39}$	30
2	21			$\overline{31}$	28	4	19	$\overline{21}$	21	$\overline{26}$	20
3	1	20	21	33	40	4	20	$\overline{7}$		2	
3	2	$\overline{72}$	66	$\overline{63}$	60	4	21			$\overline{37}$	43
3	3	$\overline{24}$	25	$\overline{41}$	43	5	1	30	28	30	
3	4	63	60	$\overline{100}$	95	5	2	$\overline{89}$	92	$\overline{51}$	58
3	5	64	69	$\overline{23}$	20	5	3	$\overline{24}$	28	$\overline{26}$	25
3	6	$\overline{8}$		19		5	4	$\overline{44}$	46	75	63
3	7	73	78	31	40	5	5	$\overline{54}$	55	42	43
3	8	5		$\overline{6}$		5	6	$\overline{4}$		$\overline{9}$	
3	9	146	147	$\overline{41}$	40	5	7	19		91	88
3	10	3		32	48	5	8	$\overline{12}$		21	
3	11	43	39	30	38	5	9	$\overline{66}$	71	85	80
3	12	$\overline{28}$		28	33	5	10	33	35	$\overline{22}$	
3	13	7		$\overline{15}$		5	11	16		60	65
3	14	$\overline{6}$		44	78	5	12	21		$\overline{34}$	35
3	15	$\overline{5}$		$\overline{38}$	35	5	13	$\overline{17}$		$\overline{10}$	
3	16	31	35	40	63	5	14	37	46	$\overline{9}$	
3	17	$\overline{11}$		55	60	5	15	$\overline{34}$	39	$\overline{29}$	35
3	18	3		$\overline{50}$	60	5	16	42	35	16	
3	19	40	32	$\overline{13}$		5	17	63	60	21	
3	20	$\overline{36}$	37	$\overline{36}$	43	5	18	$\overline{39}$	37	17	
3	21			$\overline{20}$		5	19	$\overline{23}$		18	
4	1	38	34	$\overline{3}$		5	20	$\overline{56}$	58	$\overline{32}$	33

(To be continued)

TABLE 3 (continued)

Indices		0. layer line h = 0		1. layer line h = 1		Indices		0. layer line h = 0		1. layer line h = 1	
k	l	$F_{calc.}$	$\lvert F_{obs.}\rvert$	$F_{calc.}$	$\lvert F_{obs.}\rvert$	k	l	$F_{calc.}$	$\lvert F_{obs.}\rvert$	$F_{calc.}$	$\lvert F_{obs.}\rvert$
5	21			6		8	2	14		35	33
6	1	$\overline{57}$	60	47	60	8	3	4		2	
6	2	91	85	22	28	8	4	$\overline{14}$		3	
6	3	$\overline{11}$		28	45	8	5	84	80	$\overline{34}$	
6	4	41	46	$\overline{56}$	55	8	6	$\overline{14}$		8	
6	5	$\overline{9}$		31	35	8	7	27		9	
6	6	$\overline{42}$	39	20		8	8	27	25	$\overline{14}$	
6	7	21	30	68	65	8	9	$\overline{23}$		11	
6	8	14		41	53	8	10	$\overline{10}$		26	
6	9	16		$\overline{32}$	23	8	11	$\overline{32}$	39	$\overline{19}$	
6	10	15		12	23	8	12	$\overline{19}$		$\overline{7}$	
6	11	$\overline{50}$	43	$\overline{63}$	68	8	13	$\overline{78}$	71	46	40
6	12	$\overline{15}$		1		8	14	$\overline{19}$		27	20
6	13	34	39	$\overline{17}$		8	15	$\overline{36}$	34	$\overline{16}$	20
6	14	78	76	$\overline{55}$	63	8	16	$\overline{3}$		60	68
6	15	3		$\overline{12}$		8	17	20			
6	16	66	71	16		9	1	$\overline{18}$		3	
6	17	18		4		9	2	$\overline{8}$		$\overline{7}$	
6	18	43	37	1		9	3	$\overline{18}$		27	25
6	19	$\overline{25}$	35	53	48	9	4	0		$\overline{27}$	35
6	20	48	32	$\overline{12}$		9	5	40	35	$\overline{82}$	83
7	1	36	37	34	30	9	6	14		$\overline{47}$	35
7	2	$\overline{15}$		4		9	7	77	59	6	
7	3	$\overline{65}$	50	$\overline{24}$	30	9	8	58	55	6	
7	4	2		40	53	9	9	47	43	14	
7	5	5		$\overline{58}$	68	9	10	$\overline{71}$	59	29	
7	6	74	78	50	55	9	11	43	37	$\overline{24}$	
7	7	$\overline{69}$	71	$\overline{65}$	75	9	12	$\overline{15}$		44	53
7	8	13		$\overline{41}$	43	9	13	16		$\overline{31}$	28
7	9	$\overline{51}$	55	0		9	14	27		28	28
7	10	$\overline{50}$	58	16		9	15	$\overline{17}$		6	
7	11	$\overline{22}$		$\overline{50}$	63	10	1	$\overline{55}$	35	7	
7	12	$\overline{53}$	58	$\overline{50}$	58	10	2	$\overline{76}$	60	$\overline{47}$	53
7	13	$\overline{14}$		$\overline{37}$	33	10	3	$\overline{44}$	39	$\overline{40}$	35
7	14	$\overline{7}$		$\overline{39}$	33	10	4	$\overline{1}$		$\overline{54}$	43
7	15	38		19		10	5	3		$\overline{16}$	
7	16	17		41	35	10	6	12		18	
7	17	15		11		10	7	$\overline{14}$		$\overline{33}$	
7	18	3				10	8	$\overline{16}$		15	
8	1	$\overline{5}$		$\overline{11}$		10	9	15		1	

<div align="center">TABLE 3 (continued)</div>

Indices		0. layer line $h = 0$		1. layer line $h = 1$		Indices		0. layer line $h = 0$		1. layer line $h = 1$	
k	l	F_{calc}	$\lvert F_{\text{obs}}\rvert$	F_{calc}	$\lvert F_{\text{obs}}\rvert$	k	l	F_{calc}	$\lvert F_{\text{obs}}\rvert$	F_{calc}	$\lvert F_{\text{obs}}\rvert$
10	10	13		11		12	3	$\overline{19}$	20	67	63
10	11	13		62	68	12	4	37		$\overline{36}$	28
10	12	$\overline{29}$		$\overline{5}$		12	5	$\overline{4}$		39	28
10	13	0		$\overline{11}$		12	6	31	32	$\overline{3}$	
10	14	14		$\overline{73}$	60	12	7	5		$\overline{28}$	
11	1	$\overline{19}$		4		12	8	$\overline{37}$	35		
11	2	$\overline{23}$	25	35		12	9	7			
11	3	32	23	$\overline{2}$		0	1			0	
11	4	$\overline{82}$	67	$\overline{4}$		0	3			$\overline{14}$	
11	5	$\overline{11}$		33	23	0	5			130	150
11	6	22		8		0	7			31	35
11	7	$\overline{16}$		37	35	0	9			$\overline{35}$	43
11	8	0		11		0	11			$\overline{28}$	38
11	9	$\overline{8}$		115	85	0	13			$\overline{112}$	115
11	10	10		$\overline{18}$		0	15			52	63
11	11	$\overline{20}$		16		0	17			26	35
12	1	$\overline{32}$	20	$\overline{19}$		0	19			$\overline{9}$	
12	2	51	47	$\overline{10}$		0	21			51	63

Atomic arrangement

The final atomic parameters obtained for the yellow $CsPbI_3$ are reproduced in Table 4.

Interatomic distances between atoms with parameters $(x_1\, y_1\, z_1)$ and $(x_2\, y_2\, z_2)$ have been calculated from

$$d = \left\{(x_1 - x_2)^2\, a^2 + (y_1 - y_2)^2\, b^2 + (z_1 - z_2)^2\, c^2\right\}^{1/2}$$

with $a = 4.797$ Å, $b = 10.46_2$ Å, $c = 17.78_8$ Å, and are given in Table 5. They are presumably accurate to ± 0.05 Å.

Now that the structure has been resolved it turns out to be quite similar to that of NH_4CdCl_3 and $RbCdCl_3$ investigated long ago[14, 15] only with different interatomic distances. Each Pb-atom is surrounded by six I-atoms which form a distorted octahedron and five of these I-atoms are shared by

[14] C. H. MacGillavry, H. Nijveld, S. Dierdorp, and J. Karsten, Rec. trav. chim. 58, 193 (1939).

[15] H. Brasseur and L. Pauling, J. Am. Chem. Soc. 60, 288 (1938).

TABLE 4. Atomic parameters in yellow CsPbI$_3$

All the atoms are in the special positions:

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

and for

Cs	$x = \frac{1}{4}$	$y = 0.081$	$z = 0.328$
Pb	$x = \frac{1}{4}$	$y = 0.162$	$z = 0.062$
I′	$x = \frac{1}{4}$	$y = 0.339$	$z = \overline{0.001}$
I″	$x = \frac{1}{4}$	$y = 0.031$	$z = \overline{0.114}$
I‴	$x = \frac{1}{4}$	$y = 0.298$	$z = 0.211$

two or even three octahedra so that they form bridges between the Pb-atoms. Thus the result is extended chains of Pb-I-octahedra parallel to the a-axis of the crystal. The bonding in such a polynuclear ion $(PbI_3^-)_n$ can be pictured in the following way.
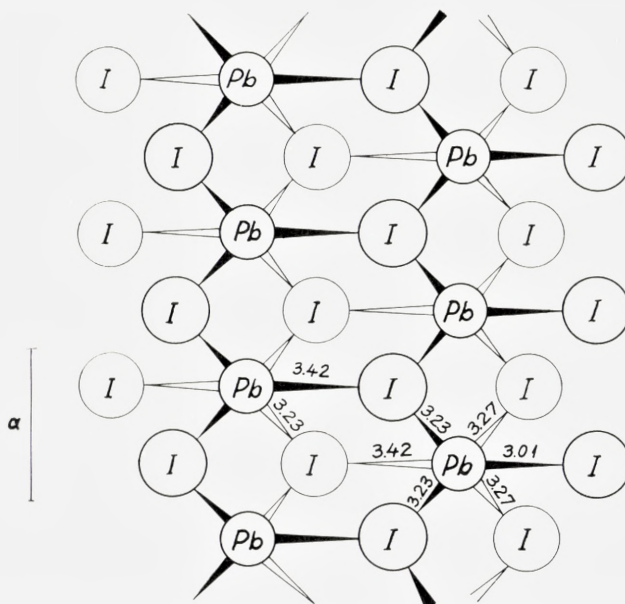

Fig. 3. $(PbI_3^-)_n$. Black, solid "bonds" point forward, light ones backward.

TABLE 5. Comparison of measured and calculated interatomic
distances in yellow $CsPbI_3$

Distance	From this investigation	From Pauling's ionic radii	From Gold-schmidt's radii
$Pb^1 — I^1$	3.23 Å	3.37 Å	3.52 Å
$Pb^1 — I^2$	3.42 -	3.37 -	3.52 -
$Pb^1 — I^3$	3.27 -	3 37 -	3.52 -
$Pb^1 — I^4$	3.01 -	3.37 -	3.52 -
$Pb^1 — Pb^2$ ...	4 70 -		
$Pb — Cs$	5.37 -		
$Cs^1 — I^5$	3.96 -	3.85 -	3.85 -
$Cs^1 — I^1$	3.99 -	3.85 -	3.85 -
$Cs^1 — I^6$	3.98 -	3.85 -	3.85 -
$Cs^1 — I^3$	4 19 -	3.85 -	3.85 -
$Cs^1 — I^4$	3.90 -	3.85 -	3.85 -
$Cs^1 — I^7$	3.87 -	3.85 -	3.85 -
$I^1 — I^1$	4.79_5 -	4.32 -	4.40 -
$I^1 — I^2$	4.49 -	4.32 -	4.40 -
$I^1 — I^3$	4.38 -	4.32 -	4.40 -
$I^1 — I^4$	4.49 -	4.32 -	4.40 -

The Cs-ions are distributed between these chains of polynuclear com-
plexes in such a way that each Cs-ion is at the centre of an almost equilateral
triangle formed by three I-atoms in the planes $x = \frac{1}{4}$ or $x = -\frac{1}{4}$; six other
I-atoms form two almost equilateral triangles below and above the one
which is co-planar with Cs, and rotated 60° with respect to this so that
Cs obtains a coordination number 9.

It would appear interesting to compare the observed interatomic distances
with those obtained from the sum of the ionic radii. However, as there are
two rather different empirical values for $r_{Pb^{++}}$, namely 1.21 Å (Pauling)
and 1.32 Å (Goldschmidt) this comparison has been made for both Pauling
and Goldschmidt ionic radii.[16]

For the Cs-I distances both sets of ionic radii give calculated distances
only slightly smaller than the observed ones. The Pb-I distances calculated
from the Goldschmidt ionic radii are considerably longer than those ob-
served and would thus indicate some "covalency" or strong polarization
of the Pb-I-bond. The Pauling radii here give expected distances closer to
the observed ones, but also in this case the calculated distance between

[16] LANDOLT BÖRNSTEIN. I. Band, 4. Teil, p. 523. Springer Verlag 1955.

Pb-atoms and the I-atoms which are not bridging the Pb-atoms is considerably longer than the measured value. This again points to strong polarization of the I-ions and it is likely that the colour of these crystals can be explained in terms hereof. That one of the Pb-I-distances is larger than expected from the Pauling radii may be explained as being due to mutual repulsion between neighbouring Pb-ions sharing I-ions.

In the earlier work on compounds of the type $MCdCl_3$ referred to above it seemed difficult to draw any definite conclusion as to whether the differences found for the Cd-Cl-distances were significant or not. Although they did show the same trend as observed here for the Pb-I-distances the differences themselves were not much larger than the uncertainty of the measurements. From the present work it can be definitely stated that the Pb-I-distances are not equal and by analogy it may be concluded that the observed differences in the Cd-Cl distances are real.

Conclusion

The result of the present investigations can be summarized by saying that divalent lead in yellow $CsPbI_3$ shows a great similarity to divalent Cd in similar compounds. Both form one-dimensional polynuclear complex ions where these metal ions have a coordination number 6 and where halogen bridging between the divalent metal ions is a characteristic feature. This type of complex ions indicates that the electrostatic attraction between the divalent ions and the halide ions is strongly modified by polarization, and it would be expected that somewhat similar complex polynuclear ions should exist also in aqueous solutions in equilibrium with these crystals.

Acknowledgments