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About the Crystal Structure of Cesium Cadmium Tribromide and Some Observations on Crystals of Cesium Cadmium Trichloride

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Dedicated to Professor K. A. Jensen on his 70th birthday

$CsCdBr_3$ forms hexagonal, optically positive crystals which contain infinite polyions $(CdBr_3^-)_n$. The polyions consist of face sharing, nearly regular $CdBr_6^{4-}$-octahedra stacked along the *c*-axis. The crystals are isomorphous to those of $RbNiCl_3$. The existence of a cubic perovskite form of $CsCdBr_3$ cannot be verified. A pure perovskite form of $CsCdCl_3$ is stable at room temperature while a hexagonal form with a structure different from that of $CsCdBr_3$ is stable at elevated temperatures.

Compounds of the composition M(I)M(II)X_3 where X is a halogen and M a metal often form crystals where the M(II)-atoms are octahedrally surrounded by X-atoms.[1] The octahedra may share corners, edges or faces of which examples are represented by $CsCdCl_3$, (cubic perovskite structure)[2,3] $RbCdBr_3$ (orthorhombic)[4] and $RbNiCl_3$ (hexagonal),[5] respectively. $CsCdBr_3$ might be expected to have a structure similar to that of $CsCdCl_3$, and it has been reported to have a cubic perovskite structure with $a = 5.33$ Å.[6] However, the density calculated on this basis is too high, 5.38 g/cm³, which is even higher than that of $CsHgBr_3$. Hence a reinvestigation of cesium cadmium bromide was considered worthwhile.

EXPERIMENTAL

Crystals of composition $CsCdBr_3$ were prepared by precipitation from aqueous solutions, *e.g.* by adding to 3.5 ml of water at room temperature 1.0 ml saturated $CdBr_2$-solution and 0.5 ml saturated CsBr-solution. The crystals were lath-shaped with pointed ends. Under the polarizing microscope they showed extinction parallel to their length and they appeared to be hexagonal and uniaxial positive, but with a rather low birefringence.

Determination of Br after Volhard and EDTA-titration of Cd showed that the crystals contained 49.9 % Br and 23.2 % Cd. (Calc. for $CsCdBr_3$: 49.4 % Br and 23.2 % Cd).

X-Ray (Guinier) powder diagrams were taken of crystals which were precipitated under very varied conditions, but they all showed the same pattern.

In order to find the conditions where the cubic form of $CsCdBr_3$ might be stable a series of solutions of CsBr or of $CdBr_2$ were prepared and to each of them crystals of the previously prepared $CsCdBr_3$ were added to form saturated solutions. The suspensions of the crystals were kept agitated in a thermostat for several days at certain well defined temperatures. For each temperature the equilibrium concentrations of Br and Cd were determined by Volhard and EDTA-titration, respectively, and the crystals in each suspension were examined optically and by X-rays (Guinier diagrams). They turned out always to be of the original, hexagonal type so that no new crystal phase was formed.

The ratio of the increase in molal concentration of Br to the increase in molal concentration of Cd, $\Delta m(\mathrm{Br}):\Delta m(\mathrm{Cd})$, on going from one temperature to a higher one was determined for each suspension (Table 1). This ratio is close to 3.0 indicating that the crystals dissolve (nearly) congruently in these solutions.

Guinier diagrams of $CsBr + CdBr_2 \cdot 4H_2O$ fused together in the stoichiometric ratio 1:1 show that the same crystalline product of $CsCdBr_3$ is obtained as from precipitation. Hence the formation of a cubic perovskite of $CsCdBr_3$ can not be confirmed from these experiments.

Crystals of composition $CsCdCl_3$ were obtained by fusing CsCl and $CdCl_2 \cdot 2\frac{1}{2}H_2O$ together in the correct stoichiometric proportion.

Table 1. Molal concentrations of Br and Cd in aqueous solutions in equilibrium with crystals of $CsCdBr_3$ at three different temperatures.

Solvent	21.0 °C		24.1 °C		29.1 °C		$\frac{\Delta m(Br)}{\Delta m(Cd)}$
	m(Br)	m(Cd)	m(Br)	m(Cd)	m(Br)	m(Cd)	
Pure water	0.807	0.265	0.883	0.293	1.015	0.336	2.9_8
0.05 M CsBr	0.782	0.242	0.858	0.273	0.982	0.311	2.8_3
0.10 M CsBr	0.743	0.217	0.836	0.248	0.960	0.299	2.7_0
0.25 M CsBr	0.716	0.167	0.822	0.197	0.934	0.243	2.8_3
0.50 M CsBr	0.793	0.119	0.885	0.153	0.988	0.189	2.8_5
1.00 M CsBr	1.199	0.103	1.257	0.128	1.380	0.168	2.8_5
0.05 M $CdBr_2$	0.850	0.287	0.911	0.315	1.023	0.354	2.6_5
0.10 M $CdBr_2$	0.884	0.308	0.956	0.336	1.085	0.385	2.7_0
0.25 M $CdBr_2$	1.022	0.406	1.112	0.454	1.205	0.474	2.7_5
0.50 M $CdBr_2$	1.372	0.612	1.460	0.639	1.552	0.683_0	2.7_0
1.00 M $CdBr_2$	2.277	1.086	2.343	1.111	2.449	1.149_0	2.7_0

X-Ray (Guinier) powder diagram of the reaction product could be indexed unambiguously on a hexagonal cell with $a = 7.41_8$ Å and $c = 18.45_4$ Å.[3,5]

On mixing dilute aqueous solutions of CsCl and $CdCl_2$ (*e.g.* 1 ml saturated CsCl-solution and 1 ml saturated $CdCl_2$-solution in 10 ml water) a white crystalline, birefringent precipitate results. The X-ray powder diagram of this has lines in common with that of $CsCdCl_3$ prepared by fusion, but in addition some other lines also. A precipitate of composition $CsCdCl_3$ was left for about three months in the mother-liquor. Then it was observed that the precipitate had lost its birefringence. An X-ray powder diagram revealed that the precipitate now consisted of crystals with ideal cubic perovskite structure with $a = 5.23_4$ Å. Thus the perovskite structure is the form of $CsCdCl_3$ which is stable at room temperature. On heating crystals of $CsCdCl_3$ having perovskite structure to about 230 °C they gradually became birefringent, and X-ray powder diagrams of the crushed crystals showed that both the cubic and the hexagonal forms were present. The transformation in the solid state appears to be very sluggish and may even commence at about 110 °C. Thus $CsCdCl_3$ is truly dimorphic.

X-Ray investigation of $CsCdBr_3$. A single crystal ($0.8 \times 0.2 \times 0.2$ mm³) of $CsCdBr_3$ grown from aqueous solution was examined by X-rays on a Weissenberg goniometer and on a precession instrument (Cu$K\alpha$-radiation). It was found to be hexagonal with the c-axis parallel to the goniometer axis. The values obtained for a and c were used for indexing Guinier diagrams of a crystalline powder of $CsCdBr_3$ and refined values could be obtained for the axes: $a = 7.68_1$ Å, $c = 6.72_6$ Å. On the assumption that the molar volumes of CsBr and $CdBr_2$ are approximately additive the unit cell is found to contain two units of formula $CsCdBr_3$. Calculated density is 4.68_6 g/cm³.

The Weissenberg photographs of the first and the third layer lines ($l = 1$ and $l = 3$) were nearly identical (apart from geometric distortion). They were generally weaker than the zeroth and second layer lines, which had many more reflections, and were definitely different from these. Also, the latter two were mutually different. Reflections of the type $h\,h\,2\bar{h}l$ were only observed for $l = 2n$. These observations comply with the space group $P6_3/mmc - D_{6h}^4$ with the two sets of metal atoms in special positions "a" and "d", the 6 bromine atoms in special positions "h",[7] (see Table 2).

Using a calibrated scale intensities were visually estimated for the zeroth and the first layer line and $|F|^2$-values were obtained after Lorentz

Table 2. Atomic positions in hexagonal $CsCdBr_3$.

2Cd:	0,0,0;	0,0,½.	
2Cs:	⅔,⅓,¼;	⅓,⅔,¾.	
6Br:	$x,2x,\frac{1}{4}$	$2\bar{x},\bar{x},\frac{1}{4}$;	$x,\bar{x},\frac{1}{4}$;
	$\bar{x},2\bar{x},\frac{3}{4}$;	$2x,x,\frac{3}{4}$;	$\bar{x},x,\frac{3}{4}$;
	$x = \frac{1}{6} = 0.167$		

Table 3. Some interatomic distances (Å) between nearest neighbours and angles (°) in hexagonal $CsCdBr_3$, z-parameters indicated.

$Cs(\frac{1}{4}) - 6Br(\frac{3}{4})$	4.03
$Cs(\frac{1}{4}) - 6Br(\frac{1}{4})$	3.84
$Cd(0) - 6Br(\pm\frac{1}{4})$	2.78
$Cd(0) - Cd(\frac{1}{2})$	3.36
$Br(\frac{1}{4}) - Br(\frac{1}{4})$ ¶	3.94
$\angle Br(\frac{1}{4}) - Cd(0) - Br(\frac{1}{4})$	87.3
$\angle Br(\frac{1}{4}) - Cd(0) - Br(\bar{\frac{1}{4}})$	92.7

Table 4. Comparison of Cd – X- and Cd – Cd-distances in different cadmium halogen compounds.

Compound	Cd – X Å	Sum of ionic radii [10] Å	Cd – Cd Å	Octahedra
K_4CdCl_6(hex) [9]	2.63	2.78	7.45	isolated
$CsCdCl_3$(cub) [3]	2.62	2.78	5.23	sharing corners
$CsCdCl_3$(hex) [3,8]	2.64;2.59	2.78	3.23	sharing faces [a]
$CsCdBr_3$(hex)	2.78	2.92	3.36	sharing faces
$RbCdBr_3$(o-rh) [4]	2.63 – 2.87	2.92	4.15	sharing edges

[a] Face-sharing as well as corner-sharing occurs in these crystals.

and polarisation corrections had been applied.

The value of the parameter x was obtained from a kind of bounded projection of the Patterson function based on the first layer line only.

Structure factor amplitudes $|F|_{calc}$ were calculated on the basis of the atomic positions given in Table 2 and atomic scattering factors from Ref. 7. The observed $|F|_{obs}$ were brought on the same scale and stripped of absorption and isotropic temperature factor.* Leaving out three strong reflections which appear definitely to have been measured too low, a reliability index $R = 0.16$ was obtained for the zeroth and first layer line together. Refinement did not seem appropriate with the present intensity data, but even so the value for the parameter x is presumably fairly accurate.

Representative interatomic distances and "bond angles" calculated on the basis of the atomic positions in Table 2 are given in Table 3. They are presumably accurate to ± 0.05 Å and 1°,respectively. $CsCdBr_3$ is thus seen to be isostructural with $RbNiCl_3$ [5] but not with hexagonal $CsCdCl_3$.[3,8]

DISCUSSION

In the crystals of $CsCdBr_3$ Cd is surrounded by 6 Br-atoms in nearly regular octahedral arrangement. These octahedra are stacked on top of one another along the c-axis, sharing the faces which are perpendicular to the c-axis. In this way linear polynuclear ions $(CdBr_3^-)_n$ result which may explain the positive birefringence and the relatively low solubility. The octahedra appear to be slightly elongated along the $\bar{3}$-axis coinciding with the c-axis.

CdX_6-octahedra occur in other cadmium halogen compounds of which some examples are given in Table 4. The Cd – X-distances in these crystals are shorter than the sum of the ionic radii of Cd^{2+} and X^-,[10] which may indicate either that the accepted ionic radius for Cd^{2+} is too long or that the shortening is due to complex formation. Accepting the latter point of view it does not seem valid to maintain that ionic radii can be deduced from crystals with the perovskite structure which often have been considered to be "ionic".

On the contrary, it may be more helpful to regard the perovskite structure as the result of the formation of a three-dimensional polynuclear complex ion consisting of CdX_6-octahedra sharing corners with the other metal ions

Table 5. Comparison of observed and calculated d-values for $CsCdBr_3$. Cu$K\alpha$-radiation, $\lambda = 1.5418$ Å.

d_o Å	d_c Å	Indices $h\,k\,l$	I_o [a]
6.67_2	6.65_2	100	vs
4.74_0	4.73_0	101	m-w
3.842	3.841	110	m-s
3.364	3.363	002	m-s
3.328	3.326	200	m-w
3.005	3.001	102	s
2.983	2.982	201	vs
2.531_3	2.530_2	112	m-w
2.515_1	2.514_3	210	m
2.365_0	2.364_9	202	vs
2.355_6	2.355_3	211	vw
2.217_1	2.217_4	300	m-w
2.123_4	2.124_6	103	vw?
2.012_7	2.013_7	212	m-s
1.919_8	1.920_3	220	m-s
1.857_7	1.859_1	203	m-s
1.843_6	1.845_0	310	vw
1.680_8	1.681_6	004	m-s
1.666_3	1.667_6	222	m

[a] Estimated intensity.

* A table of calculated and observed structure factors can be obtained from the author.

(*e.g.* Cs^+) trapped in the resulting interstices. This would be in analogy to the one-dimensional polynuclear complex ions $(CdBr_3^-)_n$ built up of face-sharing octahedra in $CsCdBr_3$ or edge-sharing ones in $RbCdBr_3$. The isolated octahedra are then represented in K_4CdCl_6.

Similar considerations could presumably be applied to many oxides with the perovskite structure.

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