

Structural studies of $\text{Cs}_2(\text{Cd}_{0.29}\text{Hg}_{0.71})\text{I}_4$ and $\text{Cs}_2(\text{Cd}_{0.34}\text{Hg}_{0.66})\text{I}_4$

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The crystals of two $\text{Cs}_2(\text{Cd}_x\text{Hg}_{1-x})\text{I}_4$ compounds have been grown from aqueous solution in the molar ratios $\text{CsI}:\text{CdI}_2:\text{HgI}_2 = 4:1:1$. They are isomorphous at room temperature and the compositions, according to the structure refinements, are $\text{Cs}_2(\text{Cd}_{0.29}\text{Hg}_{0.71})\text{I}_4$ and $\text{Cs}_2(\text{Cd}_{0.34}\text{Hg}_{0.66})\text{I}_4$ which is confirmed by SEM-EDX analyses. The triple iodides, both crystallizing in monoclinic $P2_1/m$ with average unit cell dimension $a = 7.76$, $b = 8.39$, $c = 11.03$ Å and $\beta = 110.3^\circ$, are isostructural with the room temperature phases of Cs_2CdI_4 , $a = 7.827(1)$, $b = 8.397(1)$, $c = 11.050(1)$ Å, $\beta = 110.76^\circ$, and Cs_2HgI_4 , $a = 7.734(1)$, $b = 8.386(1)$, $c = 11.019(1)$ Å, $\beta = 110.06^\circ$. The (Cd,Hg) atoms are randomly distributed in the crystals and Vegard's law is obeyed.

A large number of structural investigations of halide compounds with composition A_2BX_4 have been reported in the literature¹⁻³. Among the A_2BI_4 compounds, the monoclinic Sr_2GeS_4 -type $P2_1/m$ (ref. 4) is the predominant one. A few iodides also crystallize in the orthorhombic β - K_2SO_4 -type $Pnma$ ⁵. The accurate structure determinations of the room temperature phases α - Cs_2HgI_4 (refs. 6,7) and α - Cs_2CdI_4 (refs. 8,9) have already been reported for single crystals grown from aqueous solutions. These crystals, with almost the same cell dimensions, were both of the Sr_2GeS_4 -type. There also exist an orthorhombic high temperature phase, β - Cs_2CdI_4 , whose structure has been solved by Rietveld refinement on the basis of powder data⁸. Independently, the structure of a second room temperature modification of Cs_2CdI_4 , grown from the melt, has been reported¹⁰. This phase was of the β - K_2SO_4 -type, and identical to β - Cs_2CdI_4 (ref. 8), obtained from aqueous solution. The structural ambiguity observed between crystals grown from solution and melt-grown crystals depends on inclusion of small amounts of water (less than 0.1%) in the former, which in turn contributes to the polymorphism¹¹. However, the mechanism for this growth has not yet been completely explained. The common features for structures of Cs_2CdI_4 and Cs_2HgI_4 is a tetrahedral arrangement of I atoms around the (Cd,Hg) atoms. The I coordination around the two unique Cs ions differ slightly. In the monoclinic phase, there are 8 and 9 and in the orthorhombic phase, 9 and 11 I atoms, respectively.

Moreover, another four phases with the $\text{Cs}_2(\text{Cd,Hg})\text{I}_4$ composition exist; three modifications of Cs_2CdI_4 , grown from the melt, in the temperature range of 196 to 420 K (cell dimensions determined)¹⁰, and β - Cs_2HgI_4 (high temperature phase; d -values reported only)¹².

Earlier, we have reported structure determinations of four compounds in the $\text{CsI-MI}_2\text{-H}_2\text{O}$ system ($\text{M} = \text{Cd, Hg}$). Two of these are the room temperature phases of Cs_2CdI_4 and Cs_2HgI_4 . The present work was undertaken in order to study the effect of mixed Cd and Hg contents in $\text{Cs}_2(\text{Cd,Hg})\text{I}_4$ structures.

Materials and Methods

Single crystals were obtained by slow evaporation from an aqueous solution with molar ratios $\text{CsI}:\text{CdI}_2:\text{HgI}_2 = 4:1:1$. A number of different crystal shapes were detected; prisms, needles, plates *etc.* The crystals were transparent with slight yellow tints. Analyses of the chemical composition of various crystals were made on a scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) detecting system.

For the data collection, two crystals were picked out: one (denoted A in the following) was cut from a needle elongated along **b** with the remaining surfaces of the forms $\{1\ 0\ 0\}$ and $\{0\ 0\ 1\}$; the other one (B) was a prism with zone axis **a** and $(0\text{-}1\ 1)$, $(0\text{-}1\text{-}1)$ and $(0\ 0\ 1)$ surfaces.

Cell parameters for crystal A were obtained from a least-squares fit of 50 reflections, with 2θ ranging from 12 to 52° , collected on a locally up-

Table 1—Crystallographic data

Compound name	Cs ₂ (Cd _{0.29} Hg _{0.71})I ₄	Cs ₂ (Cd _{0.34} Hg _{0.66})I ₄
<i>M_r</i>	948.44	944.03
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>
<i>a</i> /Å	7.761(2)	7.762(2)
<i>b</i> /Å	8.388(1)	8.388(1)
<i>c</i> /Å	11.027(1)	11.026(2)
β/°	110.25(2)	110.28(2)
<i>V</i> /Å ³	673.5(2)	673.4(2)
<i>Z</i>	2	2
<i>D_x</i> /g cm ⁻³	4.692(3)	4.656(3)
<i>R</i> (000)	781	778
μ (MoK _α)/cm ⁻¹	229	220
Crystal dimensions/mm [compound A]	{100} 0.034 × {001} 0.031 × ≈ {010} 0.08 (cut)	
Crystal dimensions/mm [compound B]	{100} 0.065; (01-1) 0.031; (0-1-1) 0.034; (001) 0.05	
Grid in absorption correction	12 × 12 × 12	12 × 12 × 12
Range of transmission factor	0.20-0.33	0.13-0.27
<i>h k l</i> range	0 → 10 -11 → 11 -15 → 14	0 → 10 -11 → 11 -15 → 14
Number of reflections measured	4168	3918
Observed, <i>I</i> > 3 σ(<i>I</i>)	2293	2177
Secondary extinction coefficient (type I isotropic)	2.96(9) 10 ³	3.93(13) 10 ³
<i>R_w</i> , <i>R_σ</i>	0.043, 0.046	0.045, 0.046
<i>S</i>	0.536	3.06
(Δσ) _{max}	< 0.01	< 0.01
Δρ _{max} /Δρ _{min} (e Å ⁻³)	1.4/-1.9	1.4/-1.2

Table 2—Fractional atomic coordinates, equivalent isotropic and anisotropic temperature factors with esd's in parentheses. The anisotropic temperature factors are expressed in the form:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$$

Cs₂(Cd_{0.29}Hg_{0.71})I₄:

	x	y	z	U _{eq} (Å ²)	Occupancy	
Cd	0.0928(1)	1/4	0.2745(1)	0.0499(3)	0.292(8)	
Hg	0.0928(1)	1/4	0.2745(1)	0.0499(3)	0.708(8)	
I(1)	0.1889(2)	1/4	0.5452(1)	0.0721(6)		
I(2)	0.2596(1)	0.5139(1)	0.2121(1)	0.0551(3)		
I(3)	−0.2781(2)	1/4	0.1432(1)	0.0756(6)		
Cs(1)	0.6600(2)	1/4	0.4679(1)	0.0557(4)		
Cs(2)	0.2194(2)	1/4	0.9060(1)	0.0701(5)		
	U ₁₁ (Å ²)	U ₂₂ (Å ²)	U ₃₃ (Å ²)	U ₁₂ (Å ²)	U ₁₃ (Å ²)	U ₂₃ (Å ²)
Cd	0.0456(5)	0.0505(5)	0.0510(5)	0	0.0132(4)	0
Hg	0.0456(5)	0.0505(5)	0.0510(5)	0	0.0132(4)	0
I(1)	0.0503(7)	0.1265(13)	0.0373(6)	0	0.0124(5)	0
I(2)	0.0721(6)	0.0342(4)	0.0582(5)	−0.0029(4)	0.0215(4)	−0.0010(3)
I(3)	0.0421(7)	0.1368(14)	0.0414(6)	0	0.0060(5)	0
Cs(1)	0.0465(6)	0.0798(8)	0.0410(5)	0	0.0154(5)	0
Cs(2)	0.0745(9)	0.0771(9)	0.0415(6)	0	−0.0017(6)	0

$U_{eq} = 1/3 \sum_i \sum_j U_{ij}^* a_i a_j$, which is the equivalent isotropic factor coefficient calculated from the average of the anisotropic temperature factor over all directions.

Table 3—Selected distances (Å) and angles (°) with esd's in parentheses

$\text{Cs}_2(\text{Cd}_{0.29}\text{Hg}_{0.71})\text{I}_4$:			
(Cd,Hg)-I(3)	2.738(2)	I(3)-(Cd,Hg)-I(2)	$2 \times 111.4(1)$
(Cd,Hg)-I(2)	$2 \times 2.769(1)$	I(3)-(Cd,Hg)-I(1)	113.9(1)
(Cd,Hg)-I(1)	2.816(2)	I(2)-(Cd,Hg)-I(2)	106.2(1)
		I(2)-(Cd,Hg)-I(1)	$2 \times 106.8(1)$
Cs(1)-I(3)	3.773(2)	Cs(2)-I(3)	3.872(2)
Cs(1)-I(1)	3.892(2)	Cs(2)-I(1)	3.903(2)
Cs(1)-I(2)	$2 \times 3.904(1)$	Cs(2)-I(2)	$2 \times 3.957(1)$
Cs(1)-I(1)	4.032(2)	Cs(2)-I(2)	$2 \times 4.011(2)$
Cs(1)-I(2)	$2 \times 4.055(2)$	Cs(2)-I(3)	$2 \times 4.274(1)$
Cs(1)-I(1)	$2 \times 4.371(2)$		

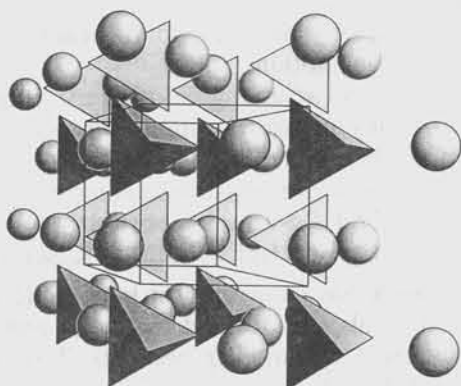


Fig. 1—Structure plot of $\text{Cs}_2(\text{Cd}_{0.29}\text{Hg}_{0.71})\text{I}_4$, viewed in perspective along $[0\ 0\ 1]$, showing unit cell packing with $(\text{Cd,Hg})\text{I}_4$ tetrahedra and Cs ions located in between. Cs(1) ions are represented by balls with black border, while Cs(2) ions are without borders. The origin is located in the upper right hand corner at the far end of the unit cell. The mirror planes are at 0.25 and 0.75 along b (vertical).

graded Nicolet P3m diffractometer¹³ with Cu K_α radiation ($\lambda = 1.541817$ Å). No further analyses were performed on the Nicolet diffractometer, due to the extremely high X-ray absorption in the A crystal. For crystal B, the cell dimensions were obtained from 25 reflections, $2\theta = 19\text{--}40^\circ$, carefully measured on a Nonius CAD4 diffractometer with graphite monochromated Mo K_α radiation ($\lambda = 0.71069$ Å).

The intensity data collections for both crystals were performed at 295 K on the Nonius CAD4 diffractometer. The software used was from Nonius CAD4¹⁴. A set of reflection data was collected upto $\theta = 30^\circ$. Scans were made in the range $\Delta\omega = 0.8^\circ + 0.35^\circ \tan \theta$ with 60 s as maximum counting time. Regular checks of orientation and intensity reflections showed no significant changes during data collection. Corrections were made for Lorentz, polarization and absorption (numerical) effects. No averaging of equivalent reflections was made.

Additional parameters used during data collection are shown in Table 1. Scattering factors for Cs^+ , Cd, Hg and I, as well as correction factors for anomalous dispersion, were taken from International Tables¹⁵.

The refinement started with x -, y - and z -coordinates obtained from refinement of α - Cs_2HgI_4 (ref. 7). Calculations were performed with programs described by Lundgren¹⁶. The function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma_c^2(F_o) + (C_1|F_o|^2 + (C_2 < |F_o| >^2)^{-1})]$. Values of (c_1, c_2) were (0.010, 0.11) and (0.010, 0.0) for A and B, respectively. In the final least-squares refinement*, anisotropic temperature factors for all atoms were assumed. Also, a correction for secondary extinction effect (isotropic type I) was included¹⁷.

Results and Discussion

In this investigation, two compounds with compositions $\text{Cs}_2(\text{Cd}_{0.29}\text{Hg}_{0.71})\text{I}_4$ and $\text{Cs}_2(\text{Cd}_{0.34}\text{Hg}_{0.66})\text{I}_4$ have been studied. The compounds are centrosymmetric, $P2_1/m$, and isostructural with α - Cs_2HgI_4 (refs. 6,7) and α - Cs_2CdI_4 (refs. 8,9). The atomic coordinates are listed in Table 2. All but one atom, I(2), are located in the mirror planes, i.e. at $y = 1/4$ and $3/4$. Each (Cd,Hg) atom is surrounded by four I atoms forming an isolated, slightly distorted, tetrahedron. Figure 1 shows the unit cell contents plotted with Cs ions and $(\text{Cd,Hg})\text{I}_4$ tetrahedra. The two independent Cs ions have eight and nine I coordination. These coordination polyhedra can be described as distorted capped trigonal prisms. In Table 3, a selection of bond lengths and angles are listed.

The occupancy factor for Hg per formula unit was refined to 0.708(8) [0.292(8) Cd] for A and to 0.658(9) [0.342(9) Cd] for B. These values

*Lists of scale factor and structure factors are available from the author on request.

were close to those achieved when Vegard's law was applied to the cell volumes, or the a cell edge, of A and B. Cell dimensions for $\alpha\text{-Cs}_2\text{HgI}_4$ (ref.7) and $\alpha\text{-Cs}_2\text{CdI}_4$ (ref. 9) are $V = 671.2(1) \text{ \AA}^3$, $a = 7.734(1)$, $b = 8.386(1)$, $c = 11.019(1) \text{ \AA}$, $\beta = 110.06^\circ$ and $V = 679.1(1) \text{ \AA}^3$, $a = 7.827(1)$, $b = 8.397(1)$, $c = 11.050(1) \text{ \AA}$, $\beta = 110.76^\circ$, respectively. The differences for b , c , and β are too small to give accurate predictions. By interpolation of the cell volumes of $\alpha\text{-Cs}_2\text{HgI}_4$ and $\alpha\text{-Cs}_2\text{CdI}_4$, values of 0.71 and 0.72 for the Hg contents were obtained, respectively.

SEM-EDX analysis on crystal A gave a value of 0.74 for the Hg/(Cd+Hg) atomic ratio when one of the crystal surfaces was analyzed. Further analyses on crystals with different shapes from the same batch as those chosen for the X-ray studies showed that the Hg/(Cd+Hg) atomic ratio varied in a wide range from 0.3 to 0.8.

A comparison of the cell volumes of $\alpha\text{-Cs}_2\text{HgI}_4$ [$671.2(1) \text{ \AA}^3$] and $\alpha\text{-Cs}_2\text{CdI}_4$ [$679.1(1) \text{ \AA}^3$], indicates that the atoms in the mercury phase are more densely packed. A closer look at the bond distances in these structures shows that on average, the Hg-I distances are only slightly longer than the Cd-I distances, as might be expected from the magnitudes of the atomic radii. However, most of the Cs-I distances are shorter in the mercury phase, which is the contributing reason why the overall packing is more dense in this phase.

It should be observed, that for the I(1) and I(3) atoms, the amplitude of thermal motion perpendicular to the mirror plane is significantly larger than within the plane. This could indicate a lower true symmetry. However, no significant decrease in the magnitudes of the thermal displacement factors were obtained with refinement in polar space group $P2_1$. The same observations were made for $\alpha\text{-Cs}_2\text{HgI}_4$ (ref. 7) and $\alpha\text{-Cs}_2\text{CdI}_4$ (ref. 9). For $\alpha\text{-Cs}_2\text{HgI}_4$, the weighted R -factor decreased from 0.0425 in space group $P2_1/m$ to 0.0416 in $P2_1$. The two alternative polar axis sensis in $P2_1$ gave almost identical R -values. However, when a split position model was tested by refinement in space group $P2_1/m$ with all atoms split along b , R_w dropped to 0.0371. The resulting splittings were 0.07(1) $\text{\AA}$ for Hg, in the range 0.12(1)-0.28(1) $\text{\AA}$ for the I atoms, and 0.03(1) and 0.18(1) $\text{\AA}$ for Cs(1) and Cs(2).

Thus, there is an indication of an unusual behaviour of the tetrahedral HgI_4^{2-} group, as of the Cs(2) ion as well, with either static or dynamic disorder across the mirror planes, or else an anharmonic thermal motion.

The $\alpha\text{-Cs}_2\text{CdI}_4$ showed similar behaviour. Here the anharmonic model was applied⁹ which resulted in as low R -factors as the split position model.

For the present crystal A, the weighted R -factor of 0.0457 for the $P2_1/m$ harmonic model decreased to 0.0433 for either absolute configuration in space group $P2_1$ and again to 0.0425 for the split position model in $P2_1/m$. The resulting splittings are: 0.25(2)-0.34(2) $\text{\AA}$ for the (Cd,Hg) and I atoms, 0.01(1) and 0.14(2) $\text{\AA}$ for the Cs(1) and Cs(2) ions, respectively.

In conclusion, it is clear that the true space group for the three phases is the centrosymmetric $P2_1/m$. The behaviour of the MI_4^{2-} group cannot yet be definitely assigned to disorder or anharmonic thermal motion.

A differential scanning calorimetry analysis did not show any phase transitions for $\alpha\text{-Cs}_2\text{HgI}_4$ or $\alpha\text{-Cs}_2\text{CdI}_4$ between 123 K and room temperature. However, there are phase transformations at 523 K to $\beta\text{-Cs}_2\text{HgI}_4$, d -values reported only¹², and at 437 K to $\beta\text{-Cs}_2\text{CdI}_4$ (ref. 8) of the $\beta\text{-K}_2\text{SO}_4$ type⁵.

This work has shown that it is possible to grow single crystals of $\text{Cs}_2(\text{Cd}_x\text{Hg}_{1-x})\text{I}_4$ compounds with different Cd and Hg contents. The distribution of Cd and Hg is probably random in the structures. Thus, it is likely that $\alpha\text{-Cs}_2\text{HgI}_4$ and $\alpha\text{-Cs}_2\text{CdI}_4$ form a continuous series of solid solutions over the entire composition range. The A and B compounds have refined parameter values very close to those obtained for the pure end phases.

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References

- Seifert H J & Stäudel L, *Z anorg allg Chem*, 429 (1977) 105.
- Zandbergen H W, Verschoor G C & Ijdo D J W, *Acta Crystallogr*, B35 (1979) 1425.
- Arend H, Murali P, Plesko S & Altermatt D, *Ferroelectrics*, 24 (1980) 297.
- Philippot E, Ribes M & Maurin M, *Rev Chimie Minér*, 8 (1971) 99.
- McGinnety J A, *Acta Crystallogr*, B28 (1972) 2845.
- Pakhomov V I & Fedorov P M, *Sov Phys Crystallogr*, 17 (1973) 833.
- Sjövall R & Svensson C, *Acta Crystallogr*, C44 (1988) 207.
- Touchard V, Louër M, Auffredic J P & Louër D, *Rev Chimie Minér*, 24 (1987) 414.
- Sjövall R, *Acta Crystallogr*, C45 (1989) 667.

- 10 Aleksandrov K S, Melnikova S V, Flerov I N, Vasilev A D, Kruglik A I & Kokov I T, *Phys Status Solidi A*, 105 (1988) 441.
- 11 Flerov I N, Gorev M V, Kot L A & Grankina V A, *Sov Phys Solid State*, 30 (1988) 1125.
- 12 Pakhomov V I, Fedorov P M, Polyakov Yu A & Kirilenko V V, *Russ J Inorg Chem*, 22 (1977) 103.
- 13 Svensson C & Sommarin B, *Acta Crystallogr*, A49 Suppl (1993) 20.
- 14 Nonius: CAD4 Software. Version 5.1. Nonius Delft, The Netherlands (1994).
- 15 *International Tables for X-ray Crystallography*, Vol 4 (Kynoch Press, Birmingham, England) 1974.
- 16 Lundgren J -O, *Crystallographic Computer Programs*. Report UUIC-B13-4-05. Institute of Chemistry, Univ. of Uppsala, Sweden (1982).
- 17 Becker P J & Coppens P, *Acta Crystallogr*, A31 (1975) 417.