

A Novel Metallic Halide, $\text{Hg}_2\text{As}_3\text{Br}$: Synthesis and Crystal Structure, and Crystal Structure of $\text{Cd}_2\text{As}_3\text{Br}$

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A new mercury arsenidobromide, $\text{Hg}_2\text{As}_3\text{Br}$, was prepared using a standard ampoule technique. It crystallizes in a monoclinic space group $C2/c$ with cell dimensions $a = 8.0914(8)$, $b = 9.300(1)$, $c = 8.1084(7)$ Å, $\beta = 99.323(0)^\circ$, $z = 4$. The structure was refined based on single crystal X-ray diffraction data to $R = 0.053$ and $R_w = 0.058$ for 739 reflections having $I > 3\sigma(I)$. $\text{Hg}_2\text{As}_3\text{Br}$ was shown to exhibit metallic conductivity from 80 K to room temperature. A redetermination of the crystal structure of $\text{Cd}_2\text{As}_3\text{Br}$ (previously reported as crystallized in space group Cc) was performed in space group $C2/c$ with cell dimensions $a = 8.281(1)$, $b = 9.411(1)$, $c = 7.993(1)$ Å, $\beta = 101.49(1)^\circ$, $z = 4$. The structure was refined to $R = 0.027$ and $R_w = 0.029$ for 485 reflections having $I > 3\sigma(I)$. Differences between the two structures are discussed. © 1994 Academic Press, Inc.

INTRODUCTION

Infinite chain anions are a common feature in the chemistry of phosphides and arsenides (1). Few examples for antimony are known (2). The compounds containing such chains exhibit a variety of electronic properties from wide gap semiconductors to semimetals. There are few pnictides containing halogens as additional anions. In $M_2P_3I_2$ ($M = \text{Cu}, \text{Ag}$) (3), phosphorus atoms form tubular chains that are structurally related to those in the Hiltorf phosphorus. Helical chains have been found in compounds with the general formula M_2P_3X , where $M = \text{Cd}, \text{Hg}$; $X = \text{Cl}, \text{Br}, \text{I}$ (except for $\text{Hg}_2\text{P}_3\text{I}$) (4, 5). Cadmium arsenidohalides with the 2 : 3 : 1 stoichiometry are also known (6, 7). The structure of the latter compounds has been refined, using X-ray powder diffraction, to poor values of R -factors. No mercury arsenidohalides of 2 : 3 : 1 stoichiometry have been reported in the literature. We attempted to prepare mercury arsenidohalides and succeeded in only one case, $\text{Hg}_2\text{As}_3\text{Br}$. The present work deals with the synthesis, crystal structure, and electrical properties of

$\text{Hg}_2\text{As}_3\text{Br}$, and the redetermination of the crystal structure of $\text{Cd}_2\text{As}_3\text{Br}$.

EXPERIMENTAL

Sample preparations were carried out in sealed silica tubes. Stoichiometric mixtures of gray arsenic, mercury (or cadmium), and respectively mercury (or cadmium) dihalides of total weight approximately 1 g were loaded into each tube. Temperature and time of annealing varied from 300°C to 550°C and from 3 to 10 days.

$\text{Hg}_2\text{As}_3\text{Br}$ was formed as black crystals of varied shape and size after annealing at 350°C for 3 days. Most of the crystals appeared in the form of parallelepipeds with maximal length 8 mm. An X-ray diffraction pattern of the product (Nonius FR-552) showed no impurities of the starting materials. All lines on a Guinier photograph were indexed in a monoclinic system by analogy with $\text{Hg}_2\text{P}_3\text{Cl}$ (5, 8). At 500°C a pure phase formed after annealing for 10 hr, but no crystals suitable for the structure determination and electrical measurements were found in the product. No phases of the 2 : 3 : 1 stoichiometry were observed in the Hg–As–Cl and Hg–As–I systems. $\text{Cd}_2\text{As}_3\text{Br}$ was synthesized at 500° for 10 hr as a black polycrystalline powder. The X-ray diffraction pattern of the product detected a pure phase.

For structure determination, suitable single crystals of $\text{Hg}_2\text{As}_3\text{Br}$ and $\text{Cd}_2\text{As}_3\text{Br}$ were selected from the respective products and mounted on CAD4 goniometer heads. Cell dimensions of $a = 8.0914(8)$, $b = 9.300(1)$, $c = 8.1084(7)$ Å, $\beta = 99.323(9)^\circ$ for $\text{Hg}_2\text{As}_3\text{Br}$ and $a = 8.281(1)$, $b = 9.411(1)$, $c = 7.993(1)$ Å, $\beta = 101.49(1)^\circ$ for $\text{Cd}_2\text{As}_3\text{Br}$ were refined based on well-centered reflections in the angular range $16^\circ < \theta < 18^\circ$. Details of data collection are summarized in Table 1. In both cases semiempirical absorption corrections were applied based on ψ -scans of four reflections; intensities were corrected for Lorentz and polarization effects.

Resistivity measurements were made on single crystals

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TABLE 1
Data Collection and Refinement Parameters

	Phase	
	Hg_2As_3Br	Cd_2As_3Br
Space group	$C2/c$ (No. 15)	$C2/c$
a (Å)	8.0914(8)	8.281(1)
b (Å)	9.300(1)	9.411(1)
c (Å)	8.1084(7)	7.993(1)
β (°)	99.323(9)	101.49(1)
V (Å ³)	602.1(1)	610.4(1)
Z	4	4
$\rho_{calc.}$ (g/cm ³)	7.786(3)	5.761(2)
μ (cm ⁻¹)	760.87	307.11
λ (MoK α)	0.71069 Å	
Temperature of measurement	293 K	
Scan mode	$\omega - 2\theta$	
$\sin \theta/\lambda_{max}$	0.745	0.616
No. of measured reflections	1186	689
No. of reflections used in refinement with $I > 3\sigma(I)$	739	485
No. of parameters refined	30	
Weights	Killean and Lawrence method (9)	
R	0.053	0.027
R_w	0.058	0.029

of Hg_2As_3Br using a standard four-probe technique between 300 and 4.2 K.

RESULTS AND DISCUSSION

Analyses of systematic absences showed that the title compounds may crystallize either in space group Cc (No. 9) or in space group $C2/c$ (No. 15). Previously reported powder diffraction refinements of the structures of Cd_2Z_3X were performed in space group Cc (6, 7). Recently we found that Hg_2P_3Cl crystallizes in space group $C2/c$ (8).

In the case of Hg_2As_3Br we located positions of all atoms by direct methods in a space group $C2/c$. A final anisotropic least-squares refinement led to $R = 0.053$ and $R_w = 0.058$, and to the atomic parameters listed in Table 2. The highest peak on the last $\Delta\rho(x, y, z)$ map was of $2.1 e \cdot \text{Å}^{-3}$, lying 0.86 Å from a mercury atom. No significant changes in atomic coordinates and residuals were observed after refinement in space group Cc .

In the case of Cd_2As_3Br we refined the structure in both possible space groups. Positions of all atoms were located by direct methods in each space group independently. Final anisotropic refinements led to $R = 0.027$, $R_w = 0.029$ in space group $C2/c$, and to $R = 0.026$, $R_w = 0.029$ in space group Cc . Atomic parameters were almost the same in both space groups. No significant changes from centrosymmetric parameters were observed in space group Cc . Previously reported atomic positions in space group Cc

TABLE 2
Atomic Parameters and Their ESDs.

Atom	Position	x/a	y/b	z/c	$B_{iso/eq}^a$
Hg_2As_3Br					
Hg1	8f	0.7250(1)	0.13322(9)	0.6603(1)	1.30(1)
Br1	4e	0	0.6354(3)	1/4	1.35(4)
As1	4e	0	0.2059(3)	1/4	0.48(4)
As2	8f	0.1303(2)	0.0597(2)	0.4842(2)	0.62(3)
Cd_2As_3Br					
Cd1	8f	0.75947(9)	0.14934(7)	0.70626(8)	1.35(1)
Br1	4e	0	0.6347(1)	1/4	1.74(3)
As1	4e	0	0.2100(1)	1/4	0.61(2)
As2	8f	0.1278(1)	0.04741(9)	0.4727(1)	0.73(2)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $\frac{1}{3} [a^2 \cdot B_{11} + b^2 \cdot B_{22} + c^2 \cdot B_{33} + a \cdot b \cdot \cos\gamma \cdot B_{12} + a \cdot c \cdot \cos\beta \cdot B_{13} + b \cdot c \cdot \cos\alpha \cdot B_{23}]$

(6) were significantly different from those found in our refinement, and could not be converted into a centrosymmetric setting. Based on these results we have chosen the centrosymmetric space group $C2/c$; atomic parameters consistent with this space group are listed in Table 2.

In the structures of M_2As_3Br ($M = Hg, Cd$) arsenic chains that spread along the c -axis of the unit cells are composed of two independent arsenic atoms (Fig. 1).

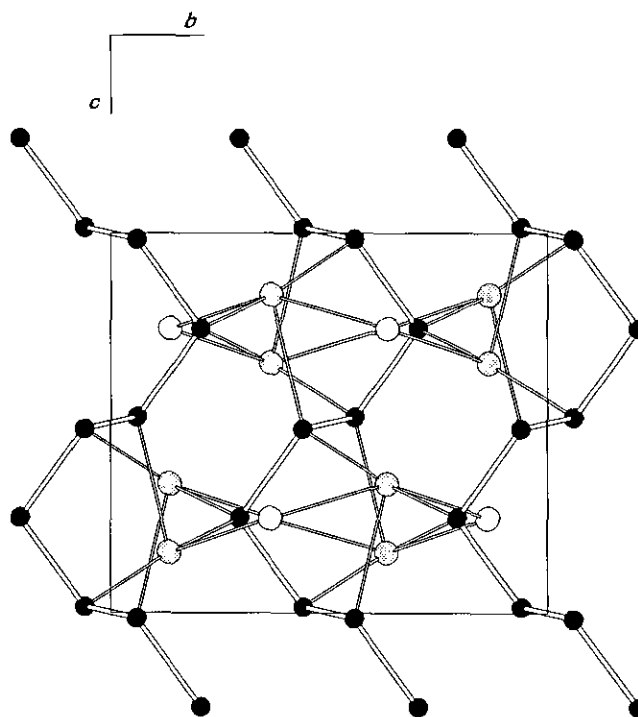


FIG. 1. Projection of the crystal structure of Hg_2As_3Br on the (100) plane. Mercury and bromine are drawn within the unit cell. Dashed circles, mercury; black circles, arsenic; open circles, bromine.

TABLE 3
Bond Distances (Å) and Bond Angles (°)

Hg ₂ As ₃ Br		
Hg1-As2 2.531(2)	Br1-Hg1-Br1	153.01(6)
As1 2.552(2)	Br1-Hg1-As1	86.30(6)
As2 3.009(2)	Br1-Hg1-As1	92.53(6)
Br1 3.096(2)	Br1-Hg1-As2	82.90(6)
Br1 3.242(3)	Br1-Hg1-As2	75.85(5)
As2-As1 2.433(3)	Br1-Hg1-As2	77.27(5)
As2 2.433(3)	Br1-Hg1-As2	103.45(6)
	As1-Hg1-As2	92.58(6)
Hg1-As2-Hg1 117.85(7)	As1-Hg1-As2	162.26(8)
Hg1-As2-As1 132.30(9)	As1-Hg1-As2	98.34(6)
Hg1-As2-As1 102.08(8)	Hg1-As1-Hg1	108.20(7)
Hg1-As2-As2 102.25(8)	Hg1-As1-As2	108.14(8) (×2)
Hg1-As2-As2 101.48(8)	Hg1-As1-As2	110.14(8) (×2)
As1-As2-As2 93.66(9)	As2-As1-As2	112.03(9)
Cd ₂ As ₃ Br		
Cd1-As2 2.623(2)	Br1-Cd1-As1	101.42(6)
As1 2.606(2)	Br1-Cd1-As2	104.91(6)
As2 2.724(2)	Br1-Cd1-As2	92.07(5)
Br1 2.819(2)	As1-Cd1-As2	145.54(6)
As2-As1 2.424(2)	As1-Cd1-As2	100.93(5)
As2 2.415(3)	As2-Cd1-As2	99.94(5)
Cd1-As2-Cd1 132.06(7)	Cd1-As1-Cd1	118.23(5)
Cd1-As2-As1 119.13(7)	Cd1-As1-As2	118.23(5) (×2)
Cd1-As2-As1 101.29(7)	Cd1-As1-As2	99.69(5) (×2)
Cd1-As2-As2 104.93(9)	As2-As1-As2	101.7(1)
Cd1-As2-As2 96.20(8)		
As1-As2-As2 95.51(9)		

These atoms each possess more or less distorted tetrahedral coordination of two mercury (or cadmium) and two arsenic atoms (Table 3). The conformation of the chains is the same as observed for phosphorus in Hg₂P₃X (X = Cl, Br) (8). The As-As distances vary in the range 2.415–2.433 Å. Similar distances are observed for polyarsenides of divalent metals that contain infinite arsenic chains. Distances of 2.413–2.437 Å, reported for ZnAs₂, are given as an example (10).

The most significant difference between the two structures is the difference in the coordination of the cadmium and mercury atoms. In Cd₂As₃Br the cadmium atom possesses a nearly regular tetrahedral coordination of one bromine and three arsenic atoms. The coordination of the mercury atom is more complicated. Mercury has two closest neighbors, As1 and As2 atoms. Three more distant atoms, 1As + 2Br, complete a highly distorted square pyramidal coordination of mercury. Figure 2 shows the arrangement of cadmium and mercury polyhedra within each structure. It is clear that cadmium-centered tetrahedra form layers separated in the *b* direction, while mercury-centered square pyramids form a three-dimensional network. Table 4 summarizes values of bonding distances

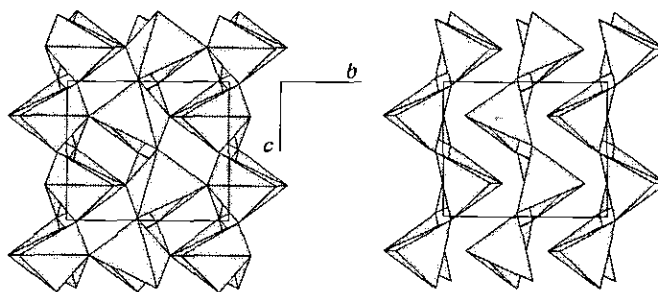


FIG. 2. Crystal structures of Hg₂As₃Br (left) and Cd₂As₃Br (right) as sequences of polyhedra. Projections on (100) planes.

that illustrate the coordination of mercury and cadmium in the 2 : 3 : 1 compounds.

Mercury has five neighbors, 3Z + 2X (X = Cl, Br; Z = P, As), in the isostructural compounds Hg₂P₃Cl and Hg₂As₃Br, and 2Z + 3X in Hg₂P₃Br. Four neighbors, 3Z + 1X, are observed for cadmium in Cd₂As₃Br, the same is true for the rest of cadmium 2 : 3 : 1 phases (4, 6, 7), though the structures of the latter compounds were refined with the lack of accuracy. The coordination of mercury and cadmium does not affect the inter-chain Z-Z distances.

The results of resistivity measurements of Hg₂As₃Br (Fig. 3) show metallic conductivity from room temperature at least down to 80 K. At this temperature resistivity is close to saturation. Prior to the measurements we expected semiconducting behavior in Hg₂As₃Br (as observed for Cd₂As₃Br). The formalization of oxidation states as (M²⁺)₂(As¹⁻)₃(Br¹⁻)₁, where M = Cd, Hg, implies semiconductivity, since all valent electrons occupy bond-

TABLE 4
Distances (Å) in Polyhedra of Mercury and Cadmium

Phase	<i>d</i> _{M-Z} ^a	<i>d</i> _{M-X}	<i>d</i> _{Z-Z}
Hg ₂ P ₃ Cl (8)	2.45	2.99	2.19
	2.46	3.04	
	2.86		
Hg ₂ P ₃ Br (8)	2.43	3.17	2.20
	2.45	3.27	
		3.34	
Hg ₂ As ₃ Br	2.53	3.10	2.43
	2.55	3.24	
	3.01		
Cd ₂ As ₃ Br	2.61	2.82	2.42
	2.62		
	2.72		

^a M = Hg, Cd; X = Cl, Br; Z = P, As.

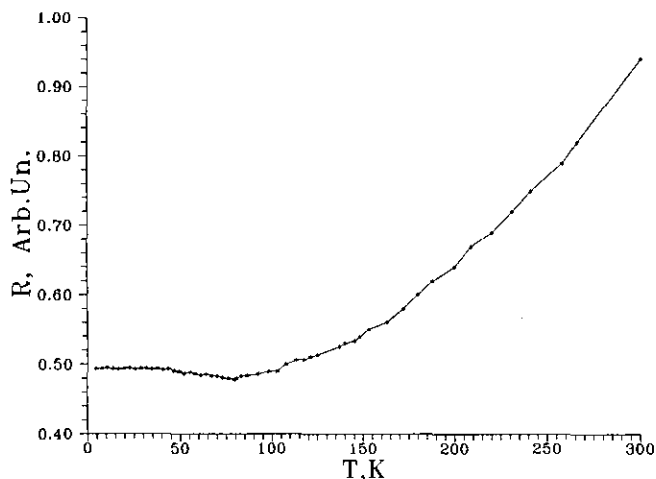


FIG. 3. Resistivity of $\text{Hg}_2\text{As}_3\text{Br}$ as a function of temperature.

ing orbitals. The metallic conductivity of $\text{Hg}_2\text{As}_3\text{Br}$ may be explained in terms of an overlapping of occupied and vacant bands, at least above 80 K. An anisotropy of resistivity in a metallic state is unlikely because of the three-dimensional arrangement of mercury polyhedra.

APPENDIX

During our attempts to synthesize a 2 : 3 : 1 phase in the Hg-As-Cl system we found a new phase that always appeared in reaction products obtained at temperatures below 350°C, together with unreacted arsenic and mercury. All lines of this phase were indexed in a cubic sys-

tem. A least-squares refinement gave unit cell parameter $a = 12.194(1) \text{ \AA}$. Taking into account that cubic symmetry is usual for mercury and cadmium pnictidohalides with the 4 : 2 : 3 stoichiometry, we hypothesized a $\text{Hg}_4\text{As}_2\text{Cl}_3$ composition for a new phase. However, our preliminary structure investigations showed that the proper composition is not $\text{Hg}_4\text{As}_2\text{Cl}_3$, but $\text{Hg}_{7.5}\text{As}_4\text{Cl}_6$, and the structure of this phase is close to that of $\text{Hg}_7\text{Sb}_4\text{Br}_6$ (11). Temperatures above 350°C always led to a partial decomposition of $\text{Hg}_{7.5}\text{As}_4\text{Cl}_6$ yielding Hg_2AsCl_2 (12) as a main product.

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