

# Cd<sub>8</sub>As<sub>7</sub>Cl: A Novel Pnictidohalide with a New Structure Type

Andrei V. Shevelkov<sup>1</sup>, Ludmila N. Reshetova, and Boris A. Popovkin

*Inorganic Synthesis Laboratory, Department of Chemistry, Moscow State University, 119899 Moscow, Russia*

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A novel cadmium arsenide chloride, Cd<sub>8</sub>As<sub>7</sub>Cl (I), has been prepared by a two-step stoichiometric synthesis. It crystallizes in the cubic space group *P*23 (No. 195) with a unit cell parameter  $a = 7.2660(10)$  Å ( $Z = 1$ ). The crystal structure has been solved based on single-crystal X-ray diffraction data ( $\omega$ - $2\theta$  scans, least-squares refinement on  $F^2$ ) to  $R = 0.0258$  and  $wR^2 = 0.0435$ . I possesses a new type of crystal structure that is described as a distorted (not dense) primitive cubic packing of cadmium atoms, the cubic voids of which are filled by either arsenic or chlorine atoms or As–As pairs. The structure of I exhibits a position disorder for one-half of the cadmium atoms. The As–As pairs are cubically surrounded by eight cadmium atoms, the As–As separation being 2.43 Å, which is longer than in all known cadmium and mercury arsenide halides. Attempts to synthesize the corresponding bromide and iodide failed. © 1997

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## INTRODUCTION

Cadmium and mercury pnictidohalides exhibit a large variety of compositions and structural types. Among them, phases containing different types of the group 15 element anions and polyanions can be found, such as  $Z^{3-}$  anions ( $Z = P, As$ ),  $Z_2^{4-}$  dumbbells ( $Z = P, As, Sb$ ), and helical  $Z^-$  chains ( $P, As$ ). A review (1) gives a survey of the pnictidohalides, with special respect to their crystal structures; further (recent) examples can be found in Refs. (2–7).  $Z_2^{4-}$  dumbbells are the most frequently observed anions. With few exceptions, the dumbbells are surrounded octahedrally by six metal atoms; exceptions are Hg<sub>5</sub>Sb<sub>2</sub>I<sub>6</sub> (6) and Hg<sub>19</sub>As<sub>10</sub>Br<sub>18</sub> (5), in which the dumbbells are surrounded by five metal atoms in such a way that octahedra with one vertex missing can be easily imagined. The  $Z$ – $Z$  distances in dumbbells do not vary much for atoms of one sort—e.g., the As–As separation falls in the short range of 2.38–2.41 Å (4, 7–10)—and these distances do not depend on the type of arrangement of octahedra in crystal structures.

In the course of our work dealing with new synthetic routes of single-crystal preparation of cadmium arsenide

halides, we have unexpectedly prepared a novel cadmium arsenide chloride, Cd<sub>8</sub>As<sub>7</sub>Cl, as a byproduct. In this article we report the synthesis of Cd<sub>8</sub>As<sub>7</sub>Cl, the phase possessing a new type of crystal structure, in which As<sub>2</sub><sup>4-</sup> dumbbells are surrounded cubically by eight cadmium atoms. Unsuccessful attempts to synthesize the respective bromide and iodide are also reported.

## EXPERIMENTAL

*Samples.* Cadmium, arsenic, and cadmium diiodide of a high purity (>99.99%) were used as received. Cadmium dichloride was prepared by heating cadmium powder under flowing HCl gas at 723 K. Cadmium dibromide was prepared by heating cadmium powder under Ar/Br<sub>2</sub> gas flow at 723 K. Cadmium dichloride and dibromide were handled and manipulated in a glovebox.

For the preparation of Cd<sub>8</sub>As<sub>7</sub>Cl, a stoichiometric mixture of cadmium, arsenic, and cadmium dichloride was sealed in a silica tube under vacuum and heated at 623 K for 3 days. The sample then was reground and heated in a sealed silica tube for 3 days at 773 K. An X-ray analysis (Enraf–Nonius FR-552 chamber, CuK $\alpha_1$  radiation) of a black air-stable product showed no traces of starting materials. All reflections were indexed in the cubic system with a unit cell parameter  $a = 7.2671(5)$  Å. The composition Cd<sub>8</sub>As<sub>7</sub>Cl was further confirmed by a crystal structure refinement.

We also attempted to synthesize the corresponding bromide and iodide. For this purpose, the stoichiometric mixtures of cadmium, arsenic, and cadmium dibromide or diiodide, respectively, were annealed under the same conditions as those for Cd<sub>8</sub>As<sub>7</sub>Cl. X-ray analysis of the products showed that they were mixtures of Cd<sub>4</sub>As<sub>2</sub>X<sub>3</sub> ( $X = Br, I$ ) and cadmium arsenides, CdAs<sub>2</sub> and Cd<sub>3</sub>As<sub>2</sub>.

*X-ray diffraction experiment.* A suitable single crystal was selected from the reaction product, glued with epoxy cement on the tip of a Pyrex fiber, and mounted on a goniometer head of a CAD-4 (Enraf–Nonius) diffractometer. Unit cell parameters were refined based on 24 well-centered reflections in the angular range of  $14^\circ < \theta < 16^\circ$ .

<sup>1</sup> To whom correspondence should be addressed.

Data were recorded at room temperature with data collection parameters listed in Table 1 and corrected for polarization and Lorentz effects. A semiempirical absorption correction was applied to data based on azimuthal scans of five reflections having their  $\chi$  angles close to 90°. Data reduction was performed using SDP programs (11).

**Crystal structure refinement.** The crystal structure of Cd<sub>8</sub>As<sub>7</sub>Cl was solved by direct methods (SHELXS-86 (12)), which revealed positions of two cadmium and two arsenic atoms. The position of the chlorine atoms was found from a Fourier map. Isotropic refinement (SHELXL-93 (13)) showed that one of two independent cadmium atoms had an enormously large thermal displacement parameter. Inspection of a difference Fourier map showed that this atom was split into two positions lying approximately 0.6 Å from each other. These two peaks were introduced into the refinement as half-occupied cadmium positions and refined isotropically to  $R = 0.0376$ . Occupancy factors of the Cd(2') and Cd(2'') atoms were then refined assuming that the sum of the factors was equal to unity (to maintain the electroneutrality). Final refinement with the anisotropic thermal displacement parameters of all atoms except for Cd(2') and Cd(2''), which were isotropic, led to  $R = 0.0258$  and the atomic parameters listed in Table 2. Selected interatomic distances and valence bond angles are listed in Table 3.

## RESULTS AND DISCUSSION

The crystal structure of Cd<sub>8</sub>As<sub>7</sub>Cl is drawn in Fig. 1, where three independent cadmium atoms are labeled. Each

**TABLE 1**  
Crystal Data and Structure Refinement for Cd<sub>8</sub>As<sub>7</sub>Cl

Unit cell parameter $a$ (Å)	7.2660(10)
Space group	$P2_3$ (No. 195)
Volume (Å <sup>3</sup> )	383.61(9)
Formula weight	1459.09
$Z$	1
$F(000)$	632
Wavelength (Å)	0.71069 (MoK $\alpha$ )
Density (calculated) (Mg/m <sup>3</sup> )	6.316
Crystal size (mm <sup>3</sup> ) and color	0.06 × 0.06 × 0.06, black
Temperature (K)	293(2)
Absorption coefficient (mm <sup>-1</sup> )	25.979
$\theta$ range for data collection (°)	2.80–24.88
Reflections collected	436
Independent reflections, $R(\text{int})$	148, 0.0517
Data/parameters	148/16
Extinction coefficient (13)	0.0039(6)
Refinement method	Full-matrix least-squares on $F^2$
Final $R$ indices ( $I > 2\sigma(I)$ )	$R_1 = 0.0258$ , $wR_2 = 0.0435^a$
$R$ indices (all data)	$R_1 = 0.0292$ , $wR_2 = 0.0445^a$
Goodness-of-fit on $F^2$	1.153
Largest diff peak and hole (e/Å <sup>3</sup> )	0.873 and $-0.687$

<sup>a</sup>  $w = 1/\sigma^2(F_o)^2$ .

**TABLE 2**  
Atomic Coordinates and Equivalent Isotropic Displacement Parameters<sup>a</sup> for Cd<sub>8</sub>As<sub>7</sub>Cl

Atom	Position	$x/a$	$y/b$	$z/c$	$U(\text{eq})^b$
Cd(1)	4e	0.2170(2)	0.2170	0.2170	0.0023(1)
Cd(2) <sup>c</sup>	4e	0.7158(6)	0.7158	0.7158	0.0023(1)
Cd(2'') <sup>c</sup>	4e	0.7637(8)	0.7637	0.7637	0.0023(1)
As(1)	1a	0	0	0	0.0014(1)
As(2)	6h	$\frac{1}{2}$	0	0.3328(2)	0.0013(1)
Cl	1b	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0020(2)

<sup>a</sup>  $U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

<sup>b</sup> Cd(2') and Cd(2'') atoms were refined isotropically.

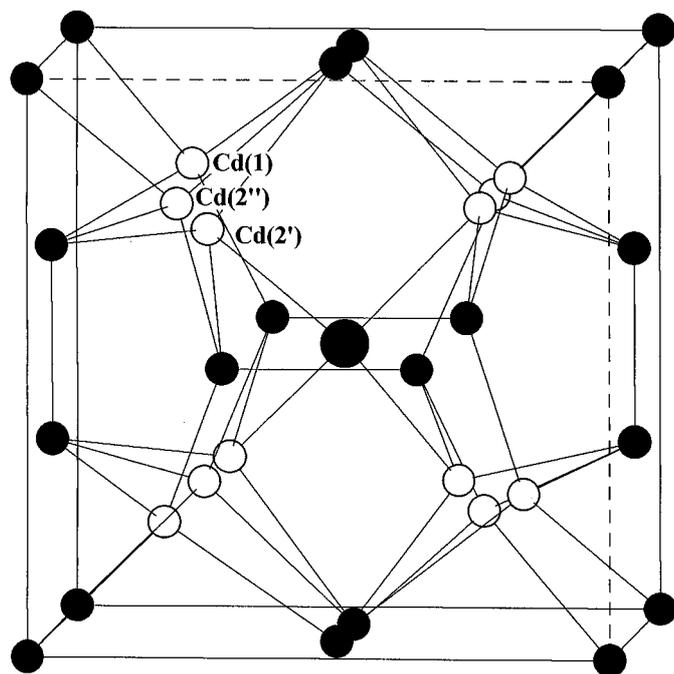
<sup>c</sup> Occupancies: 0.535(3), Cd(2'); 0.465(3), Cd(2'').

cadmium atom has a slightly distorted tetrahedral coordination, 3As(2) + 1As(1) in the cases of the Cd(1) and Cd(2'') atoms, and 3As(2) + 1Cl in the case of the Cd(2') atom. The separation between the Cd(2') and Cd(2'') positions is only 0.60 Å, which means that these atoms cannot occupy neighboring positions, but alternate randomly within the whole structure.

Since cadmium and chlorine atoms possess formal oxidation states +2 and  $-1$ , respectively, the formal charge distribution between the As(1) and As(2) atoms is evident:  $-3$  for the As(1) atoms and  $-2$  for the As(2) atoms; thus, the crystallochemical formula is written as Cd<sub>8</sub><sup>+</sup>As<sup>3-</sup>(As<sub>2</sub>)<sup>4-</sup>Cl<sup>-</sup>. The As(2) atoms are joined into As<sub>2</sub><sup>4-</sup> dumbbells, the As–As distance being 2.43 Å. Each As(2) atom is further bound to four cadmium atoms, two Cd(1) atoms and two of four randomly distributed Cd(2') and Cd(2'') atoms. The Cd–As distances vary in the range of 2.62–2.97 Å. These values exceed the normal range of the Cd–As separation in binary phases (2.53–2.58 Å in Cd<sub>3</sub>As<sub>2</sub> (14) and 2.59 Å in CdAs<sub>2</sub> (15)), as well as in cadmium arsenide halides that contain As–As pairs. In arsenide halides, such pairs are

**TABLE 3**  
Selected Interatomic Distances (Å) and Angles (°) for Cd<sub>8</sub>As<sub>7</sub>Cl

Atom–Atom	Distance	Atom–Atom–Atom	Bond angle (deg)
Cd(1)–As(2)	2.7245(9) (× 3)	As(2)–Cd(1)–As(2)	112.48(4) (× 3)
Cd(1)–As(1)	2.731(2)	As(2)–Cd(1)–As(1)	106.26(5) (× 3)
Cd(1)–Cl	3.575(2)		
Cd(2')–As(2)	2.6167(5) (× 3)	As(2)–Cd(2')–As(2)	119.90(2) (× 3)
Cd(2')–Cl	2.716(8)	As(2)–Cd(2')–Cl	91.8(2) (× 3)
Cd(2'')–As(1)	3.589(4)		
Cd(2'')–As(2)	2.667(2) (× 3)	As(2)–Cd(2'')–As(2)	116.29(13) (× 3)
Cd(2'')–As(1)	2.973(9)	As(2)–Cd(2'')–As(1)	101.2(2) (× 3)
Cd(2'')–Cl	3.284(5)		
As(2)–As(2)	2.430(3)		
Cd(2')–Cd(2'')	0.603(7)		



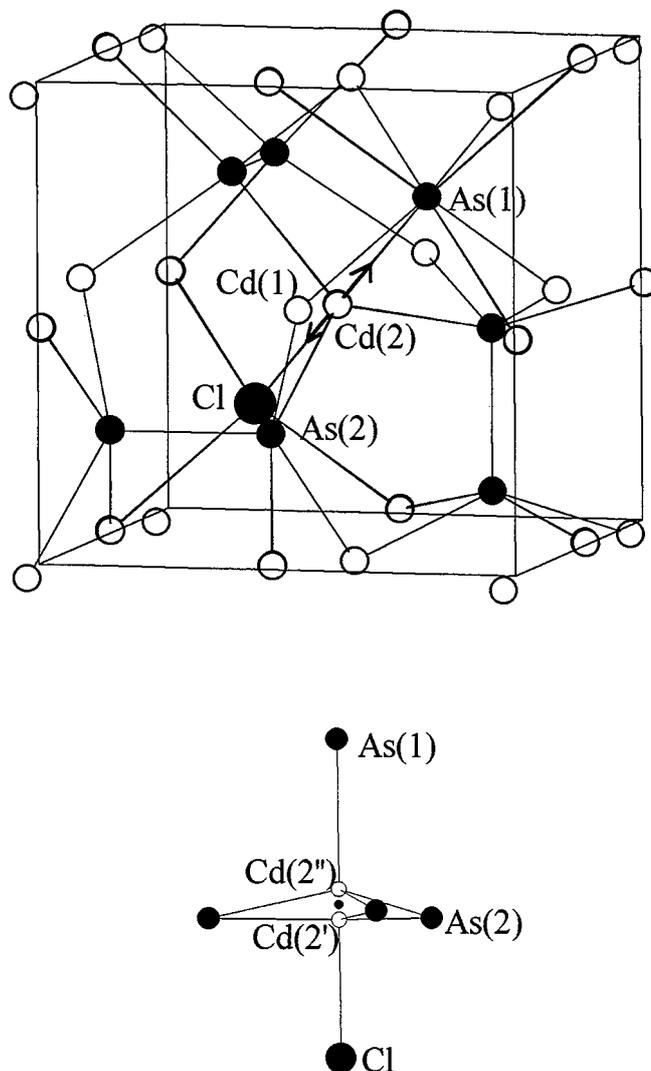
**FIG. 1.** Crystal structure of  $\text{Cd}_8\text{As}_7\text{Cl}$ : a view of the unit cell. Open circles, cadmium; smaller filled circles, arsenic; larger filled circle, chlorine. Note that the  $\text{Cd}(2')$  and  $\text{Cd}(2'')$  atoms cannot occupy the neighboring sites simultaneously due to the short  $\text{Cd}(2')\text{--Cd}(2'')$  separation of 0.603 Å.

surrounded by six cadmium atoms forming  $\text{As}_2\text{Cd}_6$  octahedra, the As–As distances ranging from 2.36 Å in  $\text{Cd}_4\text{As}_2\text{I}_3$  (8) to 2.40 Å in  $\text{Cd}_2\text{AsCl}_2$  (9). In  $\text{Cd}_8\text{As}_7\text{Cl}$ , the  $\text{As}(2)\text{--As}(2)$  pairs are surrounded by eight cadmium atoms forming a distorted cube. Such coordination of  $\text{As}_2$  pairs is very rare. One example is the high-pressure phase  $\text{CdAs}$ , in which the As–As pairs having  $d_{\text{As--As}} = 2.47$  Å are cubically surrounded by eight cadmium atoms (16).

The  $\text{As}(1)$  atom is surrounded by four  $\text{Cd}(1)$  atoms and four positions of the  $\text{Cd}(2'')$  atoms. The latter atom occupies randomly about 50% of its site; hence the  $\text{As}(1)$  atom possesses a highly distorted octahedral coordination,  $4\text{Cd}(1) + 2\text{Cd}(2'')$ . The  $\text{As}(1)\text{--Cd}$  separation is rather large (2.71 and 2.93 Å); however, there is one example,  $\text{Cd}_2\text{As}_3\text{Br}$  (4), where an arsenic atom completes its coordination with one even more distant cadmium atom ( $d_{\text{As--Cd}} = 3.00$  Å). The Cl atom is surrounded by four positions of the  $\text{Cd}(2')$  atoms. Again, since the  $\text{Cd}(2')$  atom has an about 50% occupied position, the “mean” coordination number of the Cl atom is equal to 2. The Cd–Cl distance (2.72 Å) is the same as the separation in  $\text{CdCl}_2$  (17), but slightly longer than in cadmium phosphide chlorides, 2.47–2.71 Å in  $\text{Cd}_3\text{PCl}_3$  (18) and 2.66 Å in  $\text{Cd}_7\text{P}_4\text{Cl}_6$  (19).

The crystal structure of  $\text{Cd}_8\text{As}_7\text{Cl}$  can be described as a distorted primitive cubic packing of cadmium atoms, the cubic voids of which are filled by either Cl or  $\text{As}(1)$  atoms or

$\text{As}(2)\text{--As}(2)$  pairs. Such packing can be seen in Fig. 2, where the  $\text{Cd}(2')$  and  $\text{Cd}(2'')$  atoms, each having partial occupancies, are replaced by the  $\text{Cd}(2)$  atom lying in the “ideal” position, i.e., halfway between the neighboring  $\text{Cd}(2')$  and  $\text{Cd}(2'')$  atomic sites. Figure 2 shows eight cubic voids: three voids are filled with  $\text{As}(2)\text{--As}(2)$  pairs having different orientation, one void is centered by the  $\text{As}(1)$  atom and another by the Cl atom, and three voids remain unoccupied. If half of the cadmium atoms were not split into two positions,  $\text{Cd}(2')$  and  $\text{Cd}(2'')$ , the  $\text{As}(1)$  and Cl atoms would possess coordination numbers 8 (a highly distorted cube) and 4 (a regular tetrahedron), respectively, with the following interatomic distances:  $d_{\text{As--Cd}} = 2.73$  and 3.28 Å,  $d_{\text{Cl--Cd}} =$



**FIG. 2.** (Top) A view of the crystal structure of  $\text{Cd}_8\text{As}_7\text{Cl}$ . Origin at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ . Arrows show the directions of the “ideal”  $\text{Cd}(2)$  atom split along the body diagonal of the cubic cell (cf. text). (Bottom) Coordination of the  $\text{Cd}(2')$  and  $\text{Cd}(2'')$  atoms. The small filled circle represents an ideal  $\text{Cd}(2)$  position.

3.02 Å. Such coordination would be quite unusual for both As<sup>3-</sup> and Cl<sup>-</sup> anions, and moreover, the “ideal” Cd(2) atom, if not split into Cd(2') and Cd(2'') positions, would possess an unusual trigonal-bipyramidal coordination (Fig. 2). Thus, splitting of the cadmium atomic site into two half-occupied positions affords a more convenient surrounding of the As(1) and Cl atoms and provides two tetrahedrally coordinated cadmium atoms, Cd(2') and Cd(2'').

The voids occupied by the chlorine atoms are large and seem to be suitable for incorporation of bromine atoms (instead of chlorine atoms) without any splitting of the Cd(2) atomic position. However, our attempts to prepare the corresponding bromide and iodide failed. So far, we have no reasonable explanation for this fact.

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