

# Crystal Structures of Cadmium Phosphidechlorides $\text{Cd}_7\text{P}_4\text{Cl}_6$ and $\text{Cd}_4\text{P}_2\text{Cl}_3$

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Received August 14, 1997; in revised form December 2, 1997; accepted December 15, 1997

The crystal structure of  $\text{Cd}_7\text{P}_4\text{Cl}_6$  (I) has been redetermined and of  $\text{Cd}_4\text{P}_2\text{Cl}_3$  (II) solved based on the single crystal X ray diffraction experiments. Crystal data: I, cubic space group  $Pa\bar{3}$ ,  $a = 11.936(1)$  Å,  $z = 4$ , and  $R = 0.0226$  for 398 independent reflections and 28 refined parameters; II, cubic space group  $Pa\bar{3}$ ,  $a = 12.135(1)$  Å,  $z = 8$ , and  $R = 0.0256$  for 466 independent reflections and 29 refined parameters. Both phases crystallize in a space group  $Pa\bar{3}$ , but have quite different crystal structures. The structure of I comprises a three-dimensional cationic net  $\infty^3[\text{Cd}_3\text{P}_2]^{2+}$  and discrete octahedral anions  $(\text{CdCl}_6)^{4-}$ . The structure of II is based on a fcc packing of cadmium atoms with octahedral and tetrahedral interstices filled with either chlorine or phosphorus atoms or P–P pairs. © 1998 Academic Press

## INTRODUCTION

Cadmium and mercury form a large variety of pnictohalides. There are two families of general formulas  $M_4Z_2X_3$  and  $M_{7+\delta}Z_4X_6$  ( $M = \text{Cd}, \text{Hg}$ ;  $Z = \text{P}, \text{As}, \text{Sb}$ ; and  $X = \text{Cl}, \text{Br}, \text{I}$ ) among them. The majority of these phases crystallizes in a cubic space group  $Pa\bar{3}$  with a unit cell parameter  $a$  close to 12 Å. To date more than 20 ternary  $M_4Z_2X_3$ , as well as quaternary  $M_4Z_nZ'_{2-n}X_3$  phases (so called 4:2:3 phases) are known, and most of them are reviewed in (1). The  $M_{7+\delta}Z_4X_6$  phases (so called 7:4:6 phases) are less common; only four examples are described in the literature:  $\text{Cd}_7\text{P}_4\text{Cl}_6$  (2),  $\text{Hg}_7\text{P}_4\text{Br}_6$  (3),  $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$  (4), and  $\text{Hg}_7\text{Sb}_4\text{Br}_6$  (5).

$\text{Cd}_7\text{P}_4\text{Cl}_6$  (I) and  $\text{Cd}_4\text{P}_2\text{Cl}_3$  (II) have attracted our attention as the only example of both 7:4:6 and 4:2:3 phases existing in one ternary system. This gives a good field for the structure comparison. Data show that the structure of (I) has been refined with low accuracy ( $R = 0.09$ ) (2) and the structure of (II) is unknown, although indirect evidence given in (6) such as the dimensions of a cubic cell and phase composition enable us to believe that (II) could be isomorphous to other 4:2:3 phases. In this work we report a pre-

cise crystal structure determination of (I) and (II) and discuss the differences and similarities between the two structures. Important differences between the structures of the mercury containing 7:4:6 phases and (I) are also discussed.

## EXPERIMENTAL

### Starting Materials

Cadmium (99.99%) was used as received. Red phosphorus (97%) was washed consequently with an aqueous solution of KOH (30 wt.%), ethanol and diethyl ether, and dried. Anhydrous cadmium dichloride was prepared by heating cadmium powder under flowing HCl gas at 670 K and was stored and handled in a glove box; its quality was checked by an X ray powder analysis (Nonius FR-552 chamber,  $\text{CuK}\alpha_1$  radiation).

### Single Crystals Preparation

For single crystal preparation of (I), cadmium, red phosphorus, and anhydrous cadmium dichloride were mixed in a 1:1:1 molar ratio; the mixture was heated in a sealed silica tube at 620 K for five days. The product was a mixture of different phases rich in well-shaped green crystals. An X ray pattern taken from a crop of green crystals was fully indexed in a cubic system with a unit cell parameter  $a = 11.9351(3)$  Å, which is close to the value  $a = 11.940(3)$  Å given for  $\text{Cd}_7\text{P}_4\text{Cl}_6$  in (2).

Single crystals of (II) were selected from a bulk sample prepared by a standard ampoule technique. For this, a stoichiometric mixture of cadmium, red phosphorus, and anhydrous cadmium dichloride was heated in a sealed silica tube at 770 K for 10 days. An X ray pattern of the bulk sample showed traces of impurities, while a pattern taken from a crop of selected orange crystals was fully indexed in a cubic system with a cell parameter  $a = 12.1345(3)$  Å. This value is close to the value  $a = 12.15(6)$  Å reported for  $\text{Cd}_4\text{P}_2\text{Cl}_3$  in (6).

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*X Ray Diffraction Experiments and Crystal Structures Refinement*

Selected single crystals were mounted on a goniometer head of a Nonius CAD4 diffractometer. Cubic unit cell dimensions were refined based on 24 well-centered reflections in the angular ranges  $15^\circ < \theta < 17^\circ$  (I) and  $14^\circ < \theta < 16^\circ$  (II). Data were collected at ambient temperature with data collection parameters summarized in Table 1. In both cases intensities were corrected for Lorentz and polarization effects, and semiempirical absorption corrections were applied to data based on azimuthal scans of 5 reflection having their  $\chi$  angles close to  $90^\circ$ . Data reduction was performed using SDP programs (7).

For the crystal structure refinement of (I), positions of all atoms were taken from (2). Isotropic refinement of all atomic parameters led to  $R = 0.042$ ; after that no chemically significant peaks were found on a difference Fourier map. After applying an extinction correction to data, final anisotropic refinement on  $F^2$  (8) led to  $R = 0.022$  and atomic parameters listed in Table 2.

The crystal structure of (II) was solved by direct methods (9), which located positions of two independent cadmium atoms. Consequent Fourier syntheses and least-square cycles revealed positions of the rest of the atoms. Chlorine and phosphorus atoms which have almost the same scattering power were distinguished based on their coordination, as well as on positions of pnictogen and halogen atoms in isomorphous compound Hg<sub>4</sub>As<sub>2</sub>Br<sub>3</sub> (4). Atoms were refined isotropically to  $R = 0.052$ , and then extinction correction was applied to data. Finally, atomic positions were refined anisotropically by a least-squares method on  $F^2$  (8) to  $R = 0.028$ . No chemically significant peaks were found on

**TABLE 1**  
Data Collection and Structure Refinement Parameters for Cd<sub>7</sub>P<sub>4</sub>Cl<sub>6</sub> and Cd<sub>4</sub>P<sub>2</sub>Cl<sub>3</sub>

	Cd <sub>7</sub> P <sub>4</sub> Cl <sub>6</sub>	Cd <sub>4</sub> P <sub>2</sub> Cl <sub>3</sub>
Chemical formula	Cd <sub>7</sub> P <sub>4</sub> Cl <sub>6</sub>	Cd <sub>4</sub> P <sub>2</sub> Cl <sub>3</sub>
Space group	<i>Pa</i> 3 (No. 205)	<i>Pa</i> 3 (No. 205)
Cell parameter <i>a</i> , Å	11.936(1)	12.135(1)
Volume, Å <sup>3</sup>	1700.5(2)	1787.0(3)
<i>Z</i>	4	8
Density (calc.), mg/mm <sup>3</sup>	4.388	4.593
$\mu$ , 1/mm	9.872	10.554
Crystal size, mm	0.15 × 0.12 × 0.10	0.15 × 0.13 × 0.12
Radiation, wavelength, Å	MoK $\alpha$	0.71069
$\theta$ (max.), deg.	23	24
Reflections collected	1180	1382
Independent refl. [ <i>R</i> (av.)]	398 [0.0379]	466 [0.0329]
No. of refined parameters	28	29
Extinction coefficient	0.00108(5)	0.00113(6)
<i>R</i> , <i>wR</i> <sup>2</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0226, 0.0447	0.0282, 0.0527
<i>R</i> , <i>wR</i> <sup>2</sup> (all data)	0.0256, 0.0458	0.0305, 0.0534
Largest diff. peak and hole, e/Å <sup>3</sup>	0.386 and -0.500	0.824 and -0.563
Goodness of fit on $F^2$	1.181	1.216

**TABLE 2**  
Atomic Parameters for Cd<sub>7</sub>P<sub>4</sub>Cl<sub>6</sub> and Cd<sub>4</sub>P<sub>2</sub>Cl<sub>3</sub>

Atom	Position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)
Cd <sub>7</sub> P <sub>4</sub> Cl <sub>6</sub>					
Cd(1)	24 <i>d</i>	0.23101(4)	0.01488(4)	0.27415(4)	0.0213(2)
Cd(2)	4 <i>a</i>	0	0	0	0.0205(3)
Cl	24 <i>d</i>	0.4623(1)	0.0216(1)	0.2812(1)	0.0193(3)
P(1)	8 <i>c</i>	0.2125(1)	0.2125	0.2125	0.0116(6)
P(2)	8 <i>c</i>	0.3183(1)	0.3183	0.3183	0.0107(6)
Cd <sub>4</sub> P <sub>2</sub> Cl <sub>3</sub>					
Cd(1)	8 <i>c</i>	0.72097(4)	0.22097	0.27903	0.0256(3)
Cd(2)	24 <i>d</i>	0.74978(4)	0.02669(4)	0.51212(4)	0.0239(2)
Cl	24 <i>d</i>	0.6862(1)	0.0703(1)	0.7350(1)	0.0206(4)
P(1)	8 <i>c</i>	0.9480(1)	0.0520	0.5520	0.0135(6)
P(2)	8 <i>c</i>	0.6033(1)	0.1033	0.3967	0.0147(7)

a final difference fourier map. Atomic parameters of (II) are listed in Table 2.

Selected interatomic distances and bond angles for (I) and (II) are listed in Tables 3 and 4, respectively.

### DESCRIPTION OF THE STRUCTURES

The crystal structure of (I) consists of two easily distinguished parts, octahedral anions [CdCl<sub>6</sub>]<sup>4-</sup> and a cationic three-dimensional net  $\infty^3$ [Cd<sub>3</sub>P<sub>2</sub>]<sup>2+</sup> (Fig. 1). Within the octahedral anion the Cd–Cl separation is 2.66 Å; that is slightly shorter than in an analogous octahedron in the structure of CdCl<sub>2</sub> ( $d_{\text{Cd-Cl}} = 2.72$  Å) (10). The three-dimensional net comprises three independent atoms, Cd(1), P(1), and P(2). Two independent phosphorous atoms are joined into P<sub>2</sub><sup>4-</sup> anions, the P(1)–P(2) separation being 2.19 Å. Each phosphorus atom is further bound to three Cd(1)

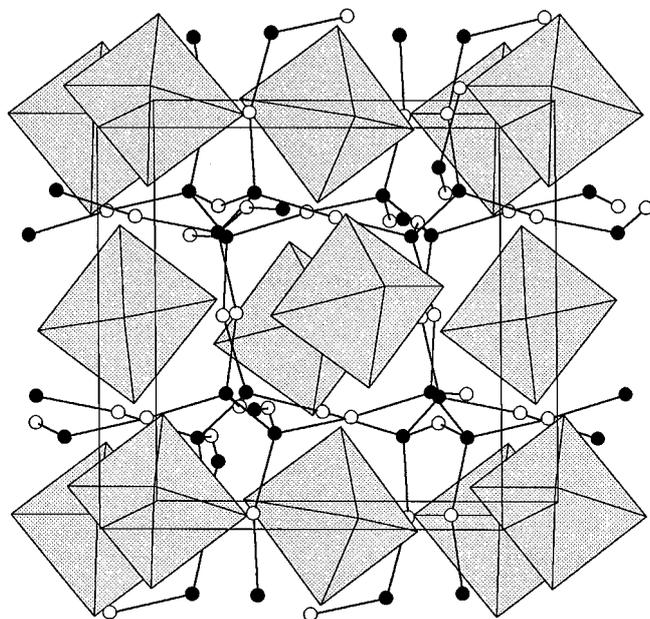
**TABLE 3**  
Selected Interatomic Distances and Bond Angles for Cd<sub>7</sub>P<sub>4</sub>Cl<sub>6</sub>

Atom–Atom	Distance, Å	Atom–Atom–Atom	Bond angle, deg.
P(1)–P(2)	2.187(4)		
Cd(2)–Cl	2.662(2) (× 6)	Cl–Cd(2)–Cl	180 (× 3)
		Cl–Cd(2)–Cl	95.05(4) (× 6)
		Cl–Cd(2)–Cl	84.95(4) (× 6)
Cd(1)–P(2)	2.4761(9)		
Cd(1)–P(1)	2.4806(9)	P(2)–Cd(1)–P(1)	160.58(6)
Cd(1)–Cl	2.761(2)	P(2)–Cd(1)–Cl	104.96(5)
		P(1)–Cd(1)–Cl	94.06(5)
Cd(1)–Cl	3.026(2)	Cd(1)–P(1)–Cd(1)	109.91(5) (× 3)
Cd(1)–Cl	3.083(2)	Cd(1)–P(1)–P(2)	109.03(5) (× 3)
Cd(1)–Cl	3.276(2)	Cd(1)–P(2)–Cd(1)	112.09(4) (× 3)
		Cd(1)–P(2)–P(1)	106.70(6) (× 3)

**TABLE 4**  
**Selected Interatomic Distances and Bond Angles for  $\text{Cd}_4\text{P}_2\text{Cl}_3$**

Atom-Atom	Distance, Å	Atom-Atom-Atom	Bond angle, deg.
P(1)-P(1)	2.187(6)		
Cd(1)-P(2)	2.474(2)	P(2)-Cd(1)-Cl	125.61(4) ( $\times 3$ )
Cd(1)-Cl	2.623(2) ( $\times 3$ )	Cl-Cd(1)-Cl	89.50(5) ( $\times 3$ )
Cd(2)-P(2)	2.4464(6)	P(2)-Cd(2)-P(1)	140.52(7)
Cd(2)-P(1)	2.4725(12)	P(2)-Cd(2)-Cl	117.52(7)
Cd(2)-Cl	2.684(2)	P(1)-Cd(2)-Cl	97.65(5)
Cd(2)-Cl	2.862(2)	P(2)-Cd(2)-Cl	105.95(5)
		P(1)-Cd(2)-Cl	93.09(6)
Cd(2)-Cl	3.560(2)	Cl-Cd(2)-Cl	84.92(2)
Cd(2)-Cl	3.647(2)		
Cd(1)-Cl	3.746(2)	Cd(2)-P(1)-Cd(2)	106.69(7) ( $\times 3$ )
		Cd(2)-P(1)-P(2)	112.13(6) ( $\times 3$ )
		Cd(1)-P(2)-Cd(2)	97.47(7) ( $\times 3$ )
		Cd(2)-P(2)-Cd(2)	118.34(3) ( $\times 3$ )

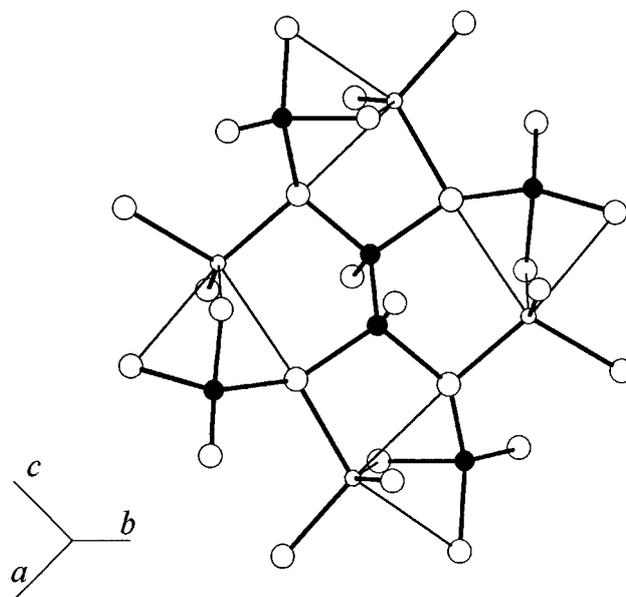
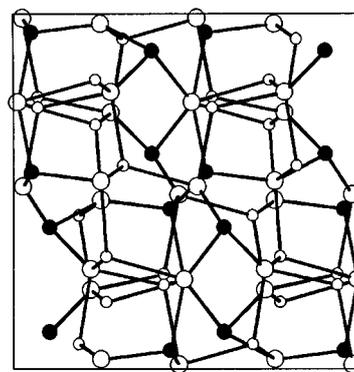
atoms forming a slightly distorted tetrahedron. Coordination of the Cd(1) atom is very unusual for cadmium. It has two close phosphorus atoms ( $d_{\text{Cd-P}} = 2.48 \text{ \AA}$ ) and is further bound to one chlorine atom at  $2.76 \text{ \AA}$ ; thus, coordination number 3 in the form of a triangle with the cadmium atom in-plane is observed. Coordination of the Cd(1) atom can be described as completed by three more distant chlorine atoms to a distorted octahedron, but the Cd-Cl distances ( $3.03, 3.08,$  and  $3.28 \text{ \AA}$ ) are too long to be bonding; they exceed the sum of the ionic radii of cadmium and chlorine



**FIG. 1.** The crystal structure of  $\text{Cd}_7\text{P}_4\text{Cl}_6$ . Open circles, cadmium; filled circles, phosphorus. The  $(\text{CdCl}_6)^{4-}$  anions are drawn as dotted octahedra.

(11). Six Cd(1) atoms surround each  $\text{P}_2^{4-}$  dumbbell; this is the base for another description of the three-dimensional net as a sequence of  $[\text{P}_2\text{Cd}_6]$  octahedra (4). Each octahedron has the center of the P-P bond at its center and shares all vertices with neighboring octahedra forming a perovskite-like framework, 1/2 of *A*-positions of which are occupied in a chess order by  $(\text{CdCl}_6)^{4-}$  anions.

The crystal structure of (II) is drawn in Fig. 2. It can be described as based on a distorted face centered cubic packing of cadmium atoms. The P(2) atoms fill 1/8 tetrahedral voids, and the P(1) atoms are joined into P-P pairs ( $d_{\text{P-P}} = 2.19 \text{ \AA}$ ) which occupy 1/8 octahedral voids. Chlorine atoms fill 3/4 octahedral voids in such a way that they are shifted from the center of octahedra toward one of the faces. Among six Cl-Cd distances there are three that can



**FIG. 2.** A view of the unit cell of the crystal structure of  $\text{Cd}_4\text{P}_2\text{Cl}_3$  (top). A fragment of the crystal structure of  $\text{Cd}_4\text{P}_2\text{Cl}_3$  (bottom). Drawn as a part of a fcc packing of cadmium atoms with chlorine and phosphorus atoms occupying tetrahedral and octahedral interstices. Large open circles, cadmium; small open circles, chlorine; filled circles, phosphorus. Thick lines, chemical bonds; thin lines, long Cd-Cl separations (cf., Table 4).

be regarded as bonding (2.62, 2.68, and 2.86 Å) and another three that are much distant (3.56, 3.65, and 3.75 Å). Figure 2 shows a fragment of a cadmium atoms packing and phosphorus and chlorine atoms which occupy the interstices. An arrangement of phosphorus and chlorine atoms provides a tetrahedral environment for cadmium atoms, 3Cl + 1P for the Cd(1) atoms, and 2P + 2Cl for the Cd(2) ones. Again, as in the case of (I), the structure of (II) can be alternatively described by subtracting [P<sub>2</sub>Cd<sub>6</sub>] octahedra based on the P(1) atoms and [PCd<sub>4</sub>] tetrahedra centered with the P(2) atoms. Two types of polyhedra comprise the three-dimensional of (II) (4).

### DISCUSSION

Compounds (I) and (II) possess quite different crystal structures, though both crystallize in a cubic space group  $Pa\bar{3}$  with close unit cell dimensions. The crystallochemical formulas [Cd<sub>3</sub>(P<sub>2</sub><sup>4-</sup>)]<sub>2</sub>(CdCl<sub>6</sub>) (I) and Cd<sub>4</sub>(P<sup>3-</sup>)<sub>2</sub>(P<sub>2</sub><sup>4-</sup>)Cl<sub>3</sub> (II) show that the two compounds differ chemically, as well as structurally. In (I) all phosphorus atoms are joined into P<sub>2</sub><sup>4-</sup> dumbbells which are surrounded octahedrally by six cadmium atoms. In (II) such dumbbells coexist with tetrahedrally coordinated phosphorus atoms in the form of P<sup>3-</sup> anions. The most striking difference is the coordination of cadmium atoms (Fig. 3). Being tetrahedrally coordinated in (II), cadmium atoms possess two different coordination polyhedra in (I), octahedral and one which is described above as triangular with the Cd atom in the plane.

It is worthy to note that the P–P distances are the same in both structures,  $d_{P-P} = 2.19$  Å, and that this distance is shorter than the interatomic distance 2.21 Å corresponding to a single P–P bond (12). Inspection of data in the literature shows that in all known cadmium and mercury phosphidehalides the P–P pairs if present have the P–P distances shorter than 2.21 Å, the only exception is Hg<sub>7</sub>P<sub>4</sub>Br<sub>6</sub>, where a distance of 2.21 Å which corresponds to a single bond is observed (3). In Hg<sub>9</sub>P<sub>5</sub>I<sub>6</sub> these values are extremely low, 2.10 and 2.13 Å (13), and that may raise a question about the bond order.

The structure of (II) looks much like the structures of other cadmium and mercury pnictidehalides having a 4:2:3 stoichiometry (1). Even Cd<sub>4</sub>P<sub>2</sub>I<sub>3</sub> (14), which exhibits an orthorhombic distortion, has the same structural motif and coordination of all atoms in the structure. On the contrary, the structure of (I) differs distinctly from the structures of Hg<sub>7</sub>P<sub>4</sub>Br<sub>6</sub> (3), Hg<sub>7</sub>Sb<sub>4</sub>Br<sub>6</sub> (5), and Hg<sub>7.4</sub>As<sub>4</sub>Cl<sub>6</sub> (4), the only known pnictidehalides of the 7:4:6 stoichiometry. While Hg<sub>7</sub>P<sub>4</sub>Br<sub>6</sub> has its special type of structure (3), Hg<sub>7</sub>Sb<sub>4</sub>Br<sub>6</sub> and Hg<sub>7.4</sub>As<sub>4</sub>Cl<sub>6</sub> crystallize in a cubic space group  $Pa\bar{3}$  and are composed each of the  $\infty^3[\text{Hg}_3\text{Z}_2]^{2+}$  cationic nets and [HgX<sub>6</sub>]<sup>4-</sup> octahedral anions (X = Cl, Br; Z = As, Sb) (4, 5). They would be isotypical with (I) if the latter had an additional metal atom in a 4b position (15). In mercury contain-

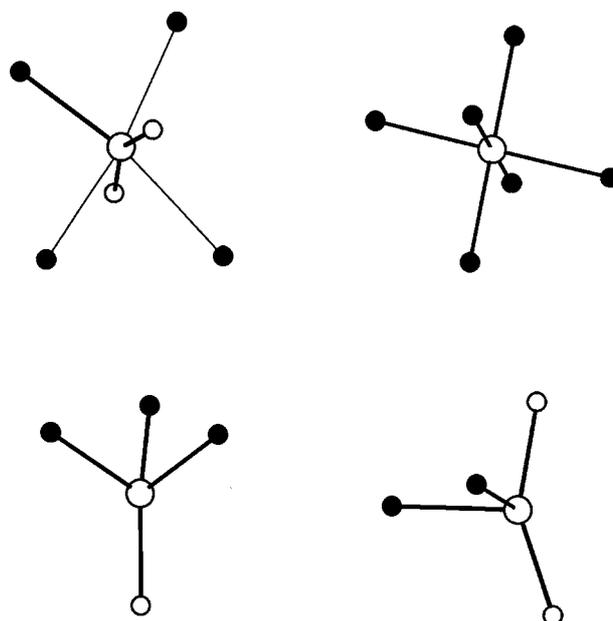


FIG. 3. Coordination of cadmium atoms: the Cd(1) atom in I (top left); the Cd(2) atom in I (top right); the Cd(1) atom in II (bottom left); and the Cd(2) atom in II (bottom right). Cadmium, large open circles; phosphorus, small open circles; chlorine, filled circles. Thin lines represent distant (more than 3 Å) Cd–Cl separations.

ing phases, mercury atoms in partially occupied 4b positions are believed to possess a zero oxidation state (4). The respective position is empty in (I); the highest Fourier peak of 0.386 e/Å<sup>3</sup> leaves no doubt about possibly unidentified atoms, and this is not a surprise. Cadmium atoms, if they had a zero oxidation state, would reduce phosphorus atoms having oxidation state –2 according to the reaction Cd<sub>7</sub>P<sub>4</sub>Cl<sub>6</sub> + Cd = 2Cd<sub>4</sub>P<sub>2</sub>Cl<sub>3</sub>. Our preliminary results show that this reaction can be easily conducted at 620 K, but this means only that at least at 620 K a thermodynamical equilibrium is achieved, and the conditions favor formation of (II). Unlike cadmium, mercury might be inserted in into (I) to occupy partially the 4b position. The relevant experiments are underway.

### ACKNOWLEDGMENTS

The authors thank Dr. Eugeny V. Dikarev (Texas A&M University) for fruitful discussions. This work is supported in part by the state program “Universities of Russia” under Grant UNI-015-95 and by the St. Petersburg Center for Basic Research under Grant 95-0-9.2-229.

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