

Crystal Structure of Hg_2PbCl_2 and Electronic Structure of Its Main "Building Unit"—The (P_2Hg_6) Octahedron

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The crystal structure of Hg_2PbCl_2 (I) has been determined based on single crystal diffraction data. I crystallizes in a monoclinic space group $I2/m$ (No. 12, a nonstandard setting), $a = 7.643(6)$ Å, $b = 7.977(2)$ Å, $c = 8.539(6)$ Å, $\beta = 115.23(3)^\circ$, $Z = 4$, $R = 0.0526$, $wR_2 = 0.1345$. Its crystal structure is based on the (P_2Hg_6) octahedron. Such octahedra share four corners out of six, forming a layer. The arrangement of the layers follows that of the K_2NiF_4 structure type. Relations of the structure of I to the structures of similar cadmium and mercury pnictidehalides are discussed. Some details of the electronic structure of I are discussed based on the molecular orbital calculations performed on a model $(\text{P}_2\text{Hg}_6)^{8+}$ cation. © 1999 Academic Press

INTRODUCTION

Ternary cadmium and mercury pnictidehalides have been investigated extensively for the past 30 years (1). Among them, the majority of compounds contains Z_2^{4-} dumbbells ($Z = \text{P, As, Sb}$) surrounded octahedrally by six metal atoms. Although compounds which contain phosphorus are the most numerous, the P_2^{4-} dumbbells surrounded by mercury have been observed only in two phases, $\text{Hg}_7\text{P}_4\text{Br}_6$ (2) and $\text{Hg}_9\text{P}_5\text{I}_6$ (3). Another compound, which according to its composition Hg_2PbCl_2 can be suspected to contain P_2^{4-} dumbbells surrounded by mercury, has been mentioned by Puff *et al.* (4,5) in the course of the systematic search for cadmium and mercury pnictidehalides. Further data showed (6) that the X-ray powder pattern was very similar to that of Hg_2AsCl_2 (7), but differed from that of Cd_2AsCl_2 (8). In this paper we report the crystal structure of Hg_2PbCl_2 , the main building unit of which is the P_2Hg_6 octahedra, and discuss differences and similarities of the structures of cadmium and mercury pnictidehalides with the 2:1:2 stoichiometry. Some features of electronic structure of the P_2Hg_6 octahedron are also discussed based on the molecular orbital calculations performed on a model $(\text{P}_2\text{Hg}_6)^{8+}$ cation.

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EXPERIMENTAL

Mercury(I) chloride Hg_2Cl_2 (>99.9%) was used as received. Red phosphorus was washed consequently by 30% aqueous solution of KOH, water, and ethanol (twice) and then vacuum dried. The starting materials were mixed in a 1:1 ratio and vacuum sealed in a silica tube. The mixture was heated at 350°C for 7 days. The product appeared as a yellow-brown polycrystalline air-stable powder. An X-ray powder diffraction pattern (Nonius FR-552, $\text{CuK}\alpha_1$ radiation) showed absence of starting materials in the sample.

A suitable yellow single crystal was selected from the product and mounted on a Nonius CAD4 goniometer head for the structure determination. Unit cell parameters $a = 7.643(6)$ Å, $b = 7.977(2)$ Å, $c = 8.539(6)$ Å, $\beta = 115.23(3)^\circ$ were refined based on 24 well-centered reflections in an angular range of $13^\circ < \theta < 16^\circ$. Data were collected at ambient temperature with data collection parameters listed in Table 1. A semiempirical absorption correction was applied to data based on ψ scans of four reflections having their χ angles close to 90° . After analysis of systematic absences, a monoclinic space group $I2/m$ (a nonstandard setting of a space group $C2/m$) was chosen for the structure refinement. Positions of mercury atoms were located from direct methods (SHELXS 86 (9)) all other atomic positions were found from subsequent least-square cycles and $\Delta\rho(x, y, z)$ syntheses. Final anisotropic refinement (SHELXL 93 (10)) was carried out by a least-square full matrix procedure on F^2 and led to $R_1 = 0.0526$ and $wR_2 = 0.135$.

RESULTS AND DISCUSSION

Atomic positions and bond distances and angles are summarized in Tables 2 and 3, respectively. A view of the crystal structure is shown in Fig. 1. The basic building unit of the structure is a Hg_6 octahedron centered with a P_2^{4-} dumbbell. The octahedra share four equatorial corners (the $\text{Hg}(2)$ atoms) to form a layer, and an arrangement of the layers follows that of the K_2NiF_4 structure type (11).

TABLE 1
Data Collection and Structure Refinement Parameters
for Hg₂PCl₂

Space group	<i>I</i> 2/ <i>m</i> (No. 12)
Unit cell dimensions, Å and deg.	<i>a</i> = 7.643(6) <i>b</i> = 7.957(2) <i>c</i> = 8.539(6) β = 115.23(3)
<i>V</i> , Å ³	469.8(5)
<i>Z</i>	4
ρ (calc.), Mg/m ³	7.113
λ , Å	0.71069
μ , mm ⁻¹	66.558
Theta range for data collection, deg.	3.00 to 25.93
Refl. collected	535
Independent refl.	502 [<i>R</i> _(int) = 0.0811]
Data/parameters	500 / 31
Extinction coeff.	0.0126(12)
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0526, <i>wR</i> ₂ = 0.1354
G-o-f on <i>F</i> ²	1.062
Largest diff. peak and hole, e ⁻ ·Å ⁻³	3.925 and -3.260

Two independent phosphorus atoms compose the P₂⁴⁻ dumbbell. Each phosphorus atom has an almost regular tetrahedral coordination of one phosphorus and three mercury atoms. The P–P distance within the P₂⁴⁻ dumbbell (2.18 Å) is almost the same as in various cadmium phosphidehalides, 2.19 Å in Cd₄P₂Cl₃ (12), Cd₄P₂I₃ (13), and Cd₇P₄Cl₆ (12), but differs from the values found in Hg₇P₄Br₆ (2.21 Å) (2) and Hg₉P₅I₆ (2.13 Å) (3).

Mercury atoms occupy two independent crystallographic positions. The Hg(1) atom is surrounded by three chlorine and one phosphorus atoms, forming a flattened tetrahedron. The Hg(2) atom is connected to two phosphorus atoms and linearly coordinated. The Hg–P distances lie in the range of 2.39–2.41 Å and are almost the same as those in Hg₇P₄Br₆ (2.40–2.44 Å). The distances Hg(1)–Cl(1) and Hg(1)–Cl(2) are 2.39 and 2.83 Å, respectively, where the Cl(1) is a terminal chlorine atom, while the Cl(2) is a bridging one. Such a description of the mercury coordination is arbitrary. There are distant chlorine atoms which may be

TABLE 2
Atomic Parameters for Hg₂PCl₂

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)
Hg(1)	0.7103(2)	0	0.2823(2)	0.019(1)
Hg(2)	1/4	1/4	1/4	0.015(1)
Cl(1)	0.8826(9)	0	0.1051(8)	0.019(1)
Cl(2)	0	0.2232(8)	1/2	0.023(2)
P	0.4432(8)	0	0.3595(7)	0.004(1)

TABLE 3
Selected Distances (Å) and Angles (deg.) in the Structure
of Hg₂PCl₂

Distances	
Hg(1)–Cl(1)	2.392(6)
Hg(1)–Cl(2)	2.829(4) (× 2)
Hg(1)–P	2.397(6)
Hg(2)–P	2.416(3) (× 2)
P–P	2.177(12)
Angles	
Cl(1)–Hg(1)–P	159.5(2)
Cl(1)–Hg(1)–Cl(2)	85.87(14) (× 2)
P–Hg(1)–Cl(2)	109.81(12) (× 2)
Cl(2)–Hg(1)–Cl(2)	77.8(2)
P–Hg(2)–P	180.0
Hg(1)–Cl(2)–Hg(1)	102.2(2)
P–P–Hg(1)	108.5(4)
P–P–Hg(2)	108.5(2) (× 2)
Hg(1)–P–Hg(2)	110.2(2) (× 2)
Hg(2)–P–Hg(2)	110.9(2)
Important nonbonding distances	
Hg(1)–Cl(2)	3.16(1) (× 2)
Hg(2)–Cl(1)	3.19(1) (× 2)
Hg(2)–Cl(1)	3.38(1) (× 2)
Hg(2)–Cl(2)	3.43(1) (× 2)

regarded as completing the mercury coordination (Fig. 2). Then, coordination of the Hg(1) atom is completed by two chlorine atoms to a very distorted octahedron, where two *cis*-Cl(2) atoms lie 3.16 Å from mercury. The same type of pseudooctahedral coordination (2 + 2 + 2) of mercury with two distant *cis*-ligands is observed in NH₄HgCl₃·H₂O (13). Coordination of the Hg(2) atom after completing by six distant chlorine atoms (*d*_{Hg–Cl} = 3.19 to 3.43 Å) becomes unusual and has never been reported in literature. All chlorine atoms reside on one plane, which is almost perpendicular to the P–Hg–P linear fragment; this coordination can be described in terms of a distorted hexagonal bipyramid.

Not only the title compound, but also Hg₂AsCl₂ (7) follows the K₂NiF₄ motif of the arrangement of Z₂M₆ octahedra. The two structures are very similar, and even the X-ray powder diffractogram of the title compound was previously indexed by analogy with Hg₂AsCl₂ (7). Our present results show that the structure of Hg₂PCl₂ is more “symmetric,” and can be solved in the space group *I*2/*m* with the unit cell volume approximately half that of Hg₂AsCl₂, which crystallizes in the space group *C*2/*m*. The transition from the body-centered to the base-centered cell is described by the matrix

$$\begin{bmatrix} 1 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix}$$

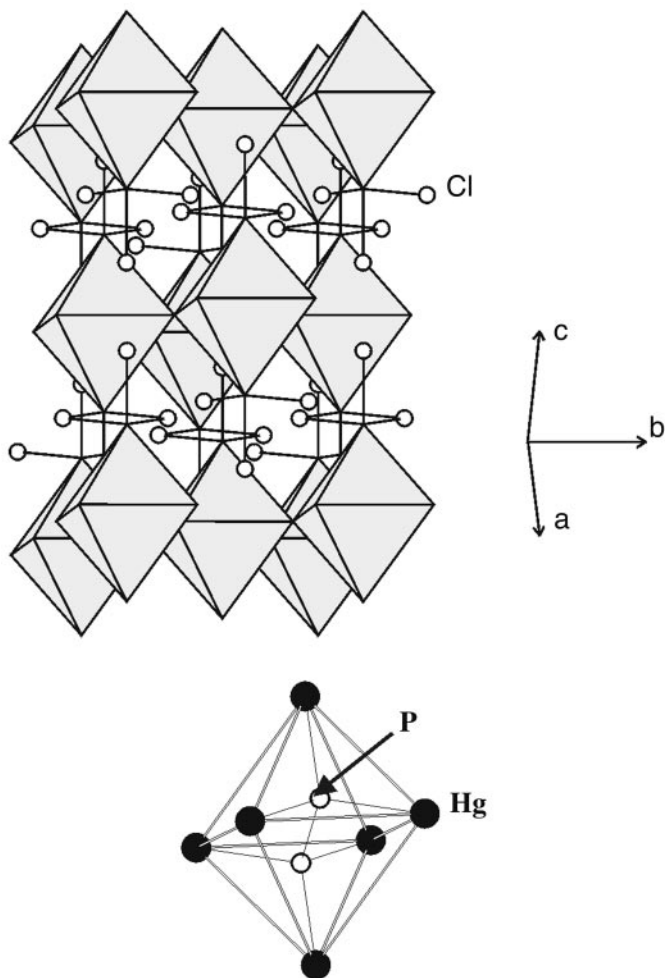


FIG. 1. A view of the crystal structure of $\text{Hg}_2\text{P}_2\text{Cl}_6$ (top) and of a (P_2Hg_6) octahedron (bottom).

In contrast to that, Cd_2AsCl_2 (8) and Cd_2SbBr_2 (15) exhibit a distorted variant of the K_2NiF_4 structure type. The trend of cadmium to achieve a tetrahedral coordination forces a twist of octahedra within a layer, as shown in Fig. 3.

Literature data show (1–3, 12, 16) that in all cadmium and mercury pnictidehalides which contain the P_2^{4-} dumbbells, such anions are surrounded by six metal atoms. Two questions arise upon analysis of these data: (i) why is the coordination of the P_2^{4-} always octahedral and never trigonal prismatic; and (ii) why are P–Cd separations always longer than P–Hg in similar compounds? To shed some light on these questions, extended Hückel calculations (17) have been performed on a model octahedral cation $(\text{P}_2\text{Hg}_6)^{8+}$ (see Computational Aspects for details). The geometry of the cation was taken from the crystal structure of $\text{Hg}_2\text{P}_2\text{Cl}_6$ and rearranged slightly to achieve idealized

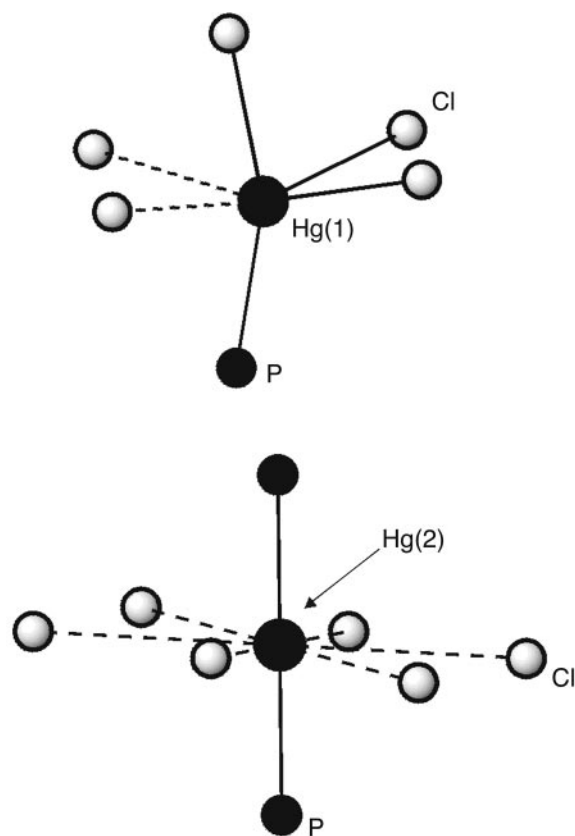


FIG. 2. Coordination of the mercury atoms in $\text{Hg}_2\text{P}_2\text{Cl}_6$. Dashed lines represent distant (not less than 3.16 Å) Hg–Cl separations, see text for details.

D_{3d} symmetry, which has been observed in several cadmium derivatives, such as $\text{Cd}_4\text{P}_2\text{Cl}_3$ (12), $\text{Cd}_4\text{P}_2\text{Br}_3$ (16), and $\text{Cd}_7\text{P}_4\text{Cl}_6$ (12). Results of calculations are shown in Fig. 4, where energy levels for the P_2^{4-} moiety are plotted for the isolated anion compared to that for the $(\text{P}_2\text{Hg}_6)^{8+}$ cation. As seen from drawings, all filled P–P orbitals lower their energy upon interacting with the Hg levels.

Analysis of P–Hg orbital interaction shows yet another two important features: (i) the e_g and e_u levels derived mainly from π orbitals of P_2^{4-} have become predominately P–Hg bonding, any significant P–P π interaction being lost; (ii) the $2a_{1g}$ and e_u levels have significant admixtures of the Hg d levels (they can be better described as s - d_{z^2} hybrids if each Hg atom resides in a local coordinate system in which the z axis points to the inversion center of the model cation). Calculations performed for comparison on the analogous model cation $(\text{P}_2\text{Cd}_6)^{8+}$ showed that the most important difference between $(\text{P}_2\text{Cd}_6)^{8+}$ and $(\text{P}_2\text{Hg}_6)^{8+}$ was that Cd d levels being too low in energy did not contribute to the $(\text{P}_2\text{Cd}_6)^{8+}$ orbitals. We believe

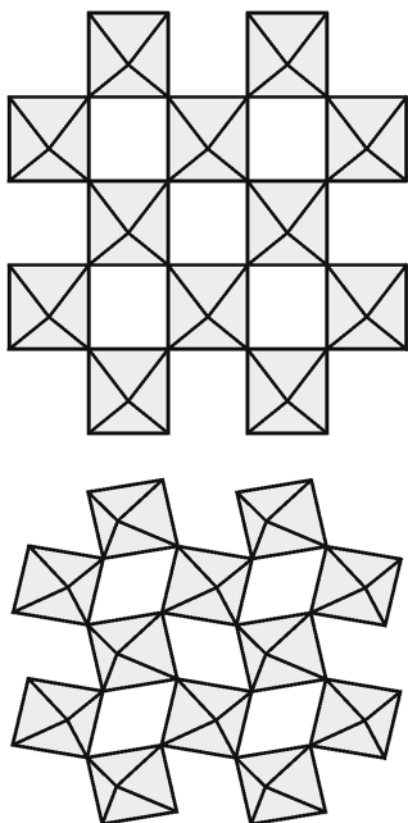


FIG. 3. A view from top on a (PHg₂) octahedral layer in the structures of Hg₂PCl₂ (top) and Cd₂SbBr₂ (bottom).

this explains why P–Cd distances are always longer than P–Hg separations in similar phases which contain the P₂⁴⁻ anion.

We have already mentioned that the P–P π bonding is lost in (P₂Hg₆)⁸⁺; consequently, the energy levels should not be sensitive to the rotation of one PHg₃ fragment about the three-fold axis. Then, rotation on a torsion angle $\tau = 60^\circ$ will lead to the trigonal prismatic (P₂Hg₆)⁸⁺ cation (D_{3h} point group), which at a first glance must have the same orbital energy as the octahedral cation. However, Fig. 5 shows a subtle increase of the total energy as a function of τ . Analysis of geometry of both cations shows that while P–P and P–Hg bond lengths and P–P–Hg and Hg–P–Hg bond angles remain the same, the Hg–Hg separation (mercury atoms from different PHg₃ units) changes from ca. 4 Å in the octahedron down to 3.52 Å in the trigonal prism. Thus, the increase of the total energy may be attributed to the Hg–Hg nonbonding repulsion. As has already been shown (17), the Hg–Hg separation of 3.35–3.45 Å makes a significant contribution to the band structures of various mercury pnictidehalides which contain phosphorus or arsenic helical chains.

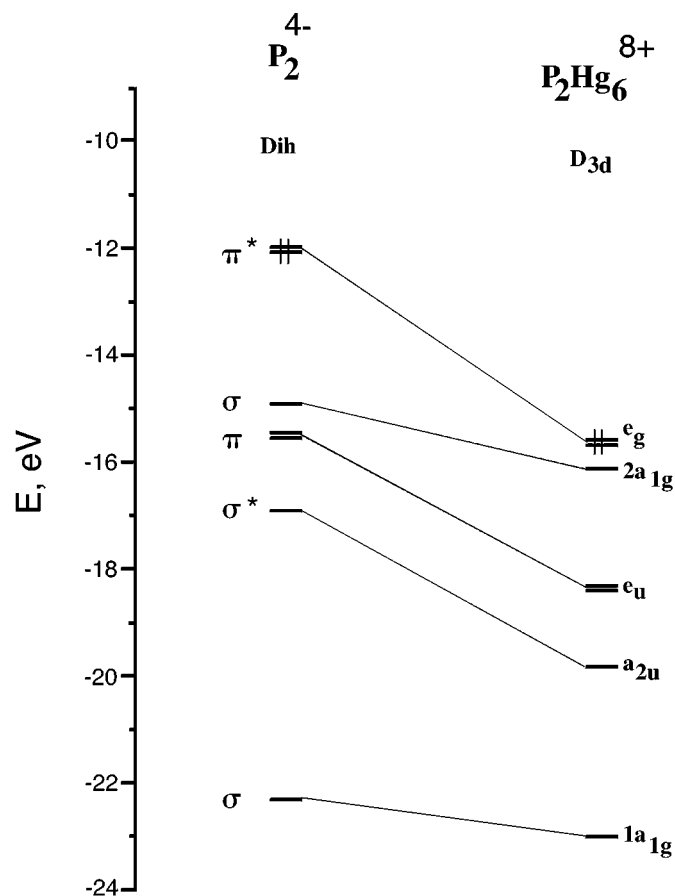


FIG. 4. Molecular orbitals diagram for P₂⁴⁻ as a separate anion (left) and in (P₂Hg₆)⁸⁺ (right). The high lying unoccupied antibonding orbitals σ^* for P₂⁴⁻ and $2a_{2u}$ for (P₂Hg₆)⁸⁺ are not shown.

It should be noted that the subtraction of the P₂Hg₆⁸⁺ cation as a model is somewhat arbitrary. The strength of P–Hg interactions should not be exaggerated since each mercury atom completes its coordination by halogen and sometimes phosphorus in different compounds. To get a complete electronic structure of phases containing such fragments, band calculations can be performed. However, such calculations unravel electronic properties of the extended structures, and may not be informative enough when some peculiarities of the main “building element” are investigated.

COMPUTATIONAL ASPECTS

Extended Hückel calculations were carried out on the model cations (P₂Cd₆)⁸⁺ and (P₂Hg₆)⁸⁺, $d(\text{P–Hg}) = 2.40 \text{ \AA}$, $d(\text{P–Cd}) = 2.45 \text{ \AA}$, $d(\text{P–P}) = 2.18 \text{ \AA}$, $\angle(\text{P–P–Hg}) = 108^\circ$, $\angle(\text{P–P–Cd}) = 108^\circ$. Atomic orbital parameters for phosphorus, cadmium, and mercury were taken from the literature (19).

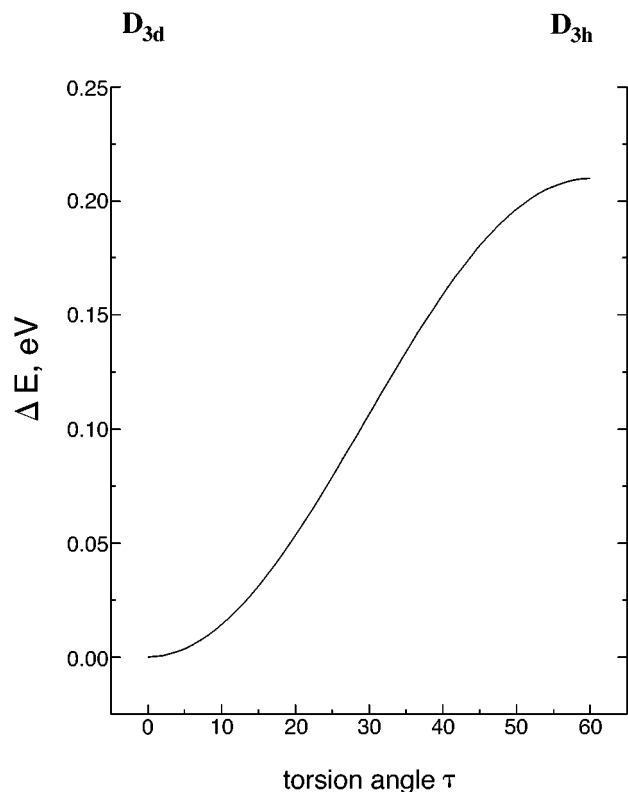


FIG. 5. Plot of ΔE as a function of the torsion angle τ in $(\text{P}_2\text{Hg}_6)^{8+}$. $\tau = 0^\circ$ for the octahedron, $\tau = 60^\circ$ for the trigonal prism.

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