JOURNAL OF SOLID STATE CHEMISTRY **104**, 177–180 (1993)

Syntheses and Crystal Structure of $Hg_7P_4Br_6$

A. V. SHEVELKOV,* E. V. DIKAREV, AND B. A. POPOVKIN

Department of Chemistry, Moscow State University, Leninskie Gory, 119899, Moscow V-234, Russia

Received May 29, 1992; accepted September 22, 1992

The mercury phosphide–bromide $Hg_7P_4Br_6$ has been synthesized and its structure has been refined based on single-crystal X-ray measurements to $R = 0.064$ and $R_w = 0.065$. The compound crystallizes in the space group $P2_1/c$ of the monoclinic system with two formula units in a cell of dimensions $a = 6.0452(7)$, $b = 19.848(2)$, $c = 7.5596(8)$ Å, and $\beta = 104.214(9)°$. The structure is built of Hg_6 octahedra filled with P_2^{4-} dumbbells. The octahedra share 5 vertices of 6 with neighboring octahedra forming a three-dimensional network. The relationship between the structures of $Hg_7P_4Br_6$ and $Hg_7Sb_4Br_6$ is discussed.

Introduction

A certain number of phases are known in the II_b–V–VII systems. As a rule, their structures appear to be complicated three-dimensional networks, where either Z_2^{4-} dumbbells (Z = P, As, Sb) (*1–5*) or infinite $^1_\infty(Z^{1-})$ chains (Z = P, As) (*6, 7*) could be subtracted. $Hg_7Sb_4Br_6$ (*8*) and $Cd_7P_4Cl_6$ (*9*) remain apart. Their structures consist of three-dimensional $[Hg_6Sb_4]$ (or $[Cd_6P_4]$) shells with holes of two different sizes. $HgBr_6$ (or $CdCl_6$) regular octahedra fill the bigger holes. Recently (*8*) we found that mercury atoms in $Hg_7Sb_4Br_6$ randomly occupied part of the $HgBr_6$ octahedra, the remaining mercury atoms being in the centers of the smaller holes. Our search for new compounds with the same stoichiometry has resulted so far in a synthesis of only one new phase, $Hg_7P_4Br_6$. We report here the crystal structure of $Hg_7P_4Br_6$, which is quite different from the structures of $Hg_7Sb_4Br_6$ and $Cd_7P_4Cl_6$. The relationship between structures with 7 : 4 : 6 stoichiometry is also discussed in this article.

Experimental

$Hg_7P_4Br_6$ was prepared by heating a stoichiometric mixture of mercury (II) bromide, red phosphorus, and liquid mercury to a temperature of 360°C in a sealed silica tube for 7 days. The X-ray analysis (Nonius FR-552, Cu$K\alpha_1$) of the product did not detect any traces of the starting materials. The composition $Hg_7P_4Br_6$ was confirmed by the structure solution.

A suitable brown crystal was selected from the reaction product and mounted on a CAD4 diffractometer. The unit cell dimensions, $a = 6.0452(7)$, $b = 19.848(2)$, $c = 7.5596(8)$ Å, $\beta = 104.214(9)°$, were refined based on 24 well-centered reflections in the angular range $16° < \theta < 18°$. Details of subsequent data collection are given in

---

* To whom correspondence should be addressed.

0022-4596/93 $5.00

TABLE I

DATA COLLECTION AND REFINEMENT PARAMETERS

Space Group	$P2_1/c$ (No. 14)
a (Å)	6.0452(7)
b (Å)	19.848(2)
c (Å)	7.5596(8)
β (°)	104.214(9)
V (Å^3)	879.3(3)
Z	2
$\rho_{\text{calc.}}$ (g/cm^3)	7.582(3)
μ (cm^{-1})	768.63
Crystal size (mm)	0.05 × 0.08 × 0.1
λ (Mo$K\alpha$)	0.71069
Temperature of measurement	293 K
Scan mode	$\omega - 2\theta$
$\sin \theta/\lambda_{\max}$	0.660
No. of measured reflections	2364
No. of reflections used in refinement with $F > 6\sigma(F)$	1286
No. of refined parameters	79
Weights	$1/w = \sigma^2(F) + 0.01F^2$
R	0.064
R_w	0.065

TABLE II

FINAL ATOMIC PARAMETERS FOR $Hg_7P_4Br_6$

Atom	x/a	y/b	z/c	$B_{\text{iso/eq}}$
Hg1	0	0	0	1.54(6)
Hg2	0.4927(3)	0.13710(8)	0.0831(2)	1.17(4)
Hg3	0.9098(3)	0.23480(8)	0.8184(2)	1.30(4)
Hg4	0.2229(3)	0.08538(9)	0.4898(2)	2.09(5)
Br1	0.4021(7)	0.0192(2)	0.7782(5)	1.20(9)
Br2	0.3604(7)	0.2122(2)	0.7012(6)	1.30(9)
Br3	0.8141(8)	0.1100(3)	0.5815(7)	2.58(13)
P1	0.145(2)	0.1017(4)	0.1654(12)	0.4(2)
P2	0.872(2)	0.1777(5)	0.0885(12)	0.5(2)

Table I. Intensities were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied based on ψ-scans of four reflections. Systematic absences, $h0l$: $l \neq 2n$, $0k0$: $k \neq 2n$, uniquely define the space group $P2_1/c$ (No. 14).

All mercury atoms were located by direct methods. The remaining atoms were found by two successive Fourier syntheses. The $\Delta\rho(x, y, z)$ syntheses that followed isotropic least-square refinement (R = 0.093, R_w = 0.096) showed the highest peak to be of 3.2 e/Å^3 lying 0.71 Å from mercury atom. Final refinement of atomic coordinates and their anisotropic thermal parameters has led to R = 0.064, R_w = 0.065, and to the atomic parameters listed in Table II. All data analysis were carried out using CSD programs (*10*).

Description of the Structure and Discussion

The crystal structure of $Hg_7P_4Br_6$ is a complicated three-dimensional framework built up from Hg, P, and Br atoms with Hg–P, Hg–Br, and P–P bonds, as is usual for the major of II_b–V–VII structures (*1–5*). The interatomic distances and bond angles are listed in Table III.

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)

Distances		Angles		
P1–P2	2.207(13)	P2–P1–Hg1	106.3(4)	
Hg1	2.423(9)	P2–P1–Hg2	111.9(4)	
Hg2	2.436(10)	P2–P1–Hg4	107.9(4)	
Hg4	2.403(9)	Hg1–P1–Hg2	109.5(4)	
		Hg1–P1–Hg4	111.7(4)	
		Hg2–P1–Hg4	109.6(4)	
P2–P1	2.207(13)	P1–P2–Hg2	115.0(5)	
Hg2	2.419(10)	P1–P2–Hg3	109.0(4)	
Hg3	2.396(9)	P1–P2–Hg3	111.5(4)	
Hg3	2.428(9)	Hg2–P2–Hg3	115.6(4)	
		Hg2–P2–Hg3	100.0(3)	
		Hg3–P2–Hg3	105.0(4)	
Hg1–P1	2.423(9) (×2)	P1–Hg1–P1	180	
Br1	3.296(4) (×2)	P1–Hg1–Br1	87.0(2)	(×2)
		P1–Hg1–Br1	93.0(2)	(×2)
		Br1–Hg1–Br1	180	
Hg2–P1	2.436(10)	P1–Hg2–P2	164.6(3)	
P2	2.419(10)			
Br1	3.236(4)			
Br1	3.286(4)			
Br2	3.173(5)			
Br2	3.276(5)			
Hg3–P2	2.396(9)	P2–Hg3–P2	159.5(3)	
P2	2.428(9)			
Br2	3.097(5)			
Br2	3.251(5)			
Br3	3.027(6)			
Hg4–P1	2.403(9)	P1–Hg4–Br1	151.4(3)	
Br1	2.548(4)	P1–Hg4–Br2	113.0(2)	
Br2	2.988(5)	P1–Hg4–Br3	105.6(3)	
Br3	2.769(5)	Br1–Hg4–Br2	88.45(13)	
		Br1–Hg4–Br3	95.45(15)	
		Br2–Hg4–Br3	82.27(14)	

The phosphorus atoms, P1 and P2, are each surrounded by one phosphorus and three mercury atoms forming an almost regular tetrahedron. The P–P distance of 2.21 Å is nearly the same as found in $Cd_4P_2I_3$ (*1*) and $Cd_7P_4Cl_6$ (*9*), but considerably longer than the shortest P–P distance of 2.10 Å in $Hg_9P_5I_6$ (*11*), and corresponds to the single P–P bond (*12*). The P–Hg distances (2.40–2.44 Å) correlate well with those in $Hg_9P_5I_6$. The P–P contact of 2.21 Å and the tetrahedral coordination of phosphorus, 1P + 3Hg, define the P_2^{4-} dumbbell previously described in the structures of II_b–V–VII series (*1, 9, 11*).

The coordination of four independent mercury atoms is more complex. The Hg1 atom possesses unusual planar coordination. Two phosphorus atoms (in *trans* form) and two more distant bromine atoms build a parallelogram. The Hg2 atom is surrounded by two phosphorus atoms; four more distant bromine atoms complete the distorted octahedral coordination. The Hg3 atom is surrounded by two phosphorus and three bromine atoms, forming a highly distorted trigonal bipyramid. Finally, the Hg4 atom is situated at the center of a distorted tetrahedron of three bromine and one phosphorus atoms. When compared with the structures of II_b–V–VII series, the coordination of Hg2, Hg3, and Hg4 atoms is quite usual; on the other hand, the Hg1 atom possesses unique coordination.

The Hg–Br distances vary in the range 2.55–3.30 Å, depending on the coordination of the mercury atoms. The Hg4 atom with 1P + 3Br neighborhood has shorter Hg–Br distances than Hg1, Hg2, and Hg3 atoms with 2P + 2Br, 2P + 4Br, and 2P + 3Br neighborhoods, respectively.

The shortest Hg–Hg and P–Br contacts are larger than the sums of the corresponding van der Waals radii. The shortest Br–Br distance of 3.36 Å is slightly smaller than the sum of the bromine van der Waals radii. Still, no Hg–Hg, P–Br, and Br–Br bonding can be considered, and the compound can be formulated as $[(Hg^{2+})_7(P_2^{4-})_2(Br^{1-})_6]$.

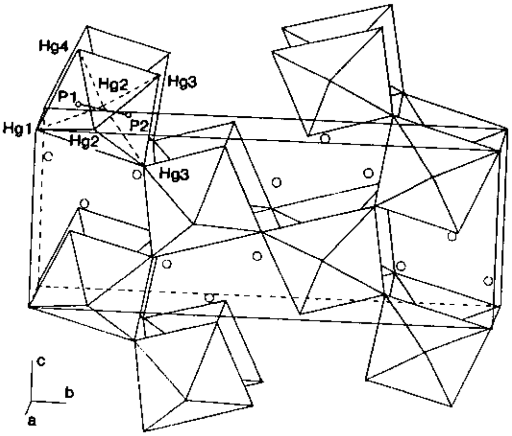

FIG. 1. A view of the crystal structure of $Hg_7P_4Br_6$ down the *a* axes. Three-dimensional sequences of P_2Hg_6 octahedra are shown. Bromine atoms are drawn inside the unit cell with circles. A P_2^{4-} dumbbell is drawn in the top left corner.

The arrangement of mercury atoms can be described in terms of distorted Hg_6 octahedra centered with P_2^{4-} dumbbells. Figure 1 presents the structure of $Hg_7P_4Br_6$ as a compilation of corner-shared Hg_6P_2 octahedra with bromine atoms in between. Each octahedron shares 5 vertices of 6 with neighboring octahedra, while one vertex remains unshared.

Though the structure of $Hg_7P_4Br_6$ is quite different from those of isomorphous $Hg_7Sb_4Br_6$ (*8*) and $Cd_7P_4Cl_6$ (*9*) compounds, the relationship between two structure types can easily be found (Fig. 2). When the octahedra are turned round a pseudo-4-fold axis running through the Hg2 atoms, the unshared vertices, Hg4 atoms, collide (shown in Fig. 2a with arrows), and a three-dimensional $[Hg_6P_4]$ framework with all vertices shared is formed. That leads to a "perovskite-like" sequence of octahedra with one half of the A-positions occupied in an orderly way by $HgBr_6$ (or $CdCl_6$) octahedra in the structures of $Hg_7Sb_4Br_6$ (or $Cd_7P_4Cl_6$)

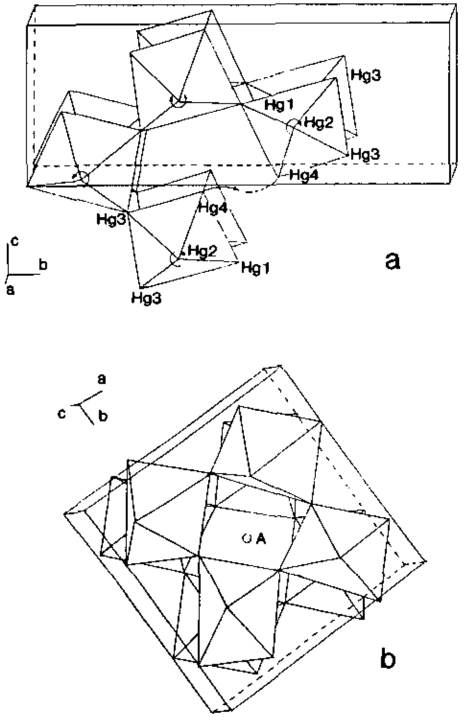

FIG. 2. The relationship between the strctures of $Hg_7P_4Br_6$ (a) and $Hg_7Sb_4Br_6$ (b). See text for explanations.

(Fig. 2b). In the case of $Hg_7P_4Br_6$, the $HgBr_6$ octahedra are too large to occupy A-positions, which could be a reason why $Hg_7P_4Br_6$ does not crystallize in the structure type of $Hg_7Sb_4Br_6$.

The dimensions of the M_6 (M = Cd, Hg) octahedron are obviously determined by the covalent radius of the V group element, and therefore, by the Z–Z distance in the Z_2^{4-} dumbbell (Z = P, As, Sb). The consistency of the dimensions of Z_2^{4-} centered M_6 octahedra and MX_6 octahedra (X = Cl, Br) is necessary for the stability of the $Hg_7Sb_4Br_6$ structure type. Taking into account the similarity of the respective Hg–Z and Cd–Z distances, as well as the Hg–X and Cd–X distances, in II_b–V–VII compounds, one can predict the existence of $Cd_7Sb_4Br_6$ and $Hg_7P_4Cl_6$ phases, but as yet we have failed to obtain the compounds with the mentioned compositions.

References

1. A. REBBAH, J. YAZBECK, AND A. DESCHANVRES, *Acta Crystallogr. Sect. B* **36,** 1747 (1980).
2. J. GALLAY, A. ALLAIS, AND A. DESCHANVRES, *Acta Crystallogr. Sect. B* **31,** 2274 (1975).
3. PH. LABBÉ, M. LEDÉSERT, B. RAVEAU, AND A. REBBAH, *Z. Kristallogr.* **187,** 117 (1989).
4. A. V. SHEVELKOV, E. V. DIKAREV, AND B. A. POPOVKIN, *J. Solid State Chem.* **93,** 331 (1991).
5. A. REBBAH, J. YAZBECK, A. LECLAIRE, AND A. DESCHANVRES, *Acta Crystallogr. Sect. B* **36,** 771 (1980).
6. A. REBBAH, J. YAZBECK, R. LANDE, AND A. DESCHANVRES, *Mater. Res. Bull.* **16,** 525 (1981).
7. A. REBBAH, A. LECLAIRE, J. YAZBECK, AND A. DESCHANVRES, *Acta Crystallogr. Sect. B* **35,** 2197 (1979).
8. A. V. SHEVELKOV, E. V. DIKAREV, AND B. A. POPOVKIN, *J. Solid State Chem.* **98,** 133 (1992).
9. A. REBBAH, J. YAZBECK, AND A. DESCHANVRES, *Rev. Chim. Miner.* **17,** 96 (1980).
10. L. G. AKSELRUD, YU. N. GRYN, P. YU. ZAVALIY, V. K. PECHARSKY, AND V. S. FUNDAMENTSKY, "Report on the 12th European Crystallographic Meeting, Moscow," p. 155 (1989).
11. M. LEDÉSERT, A. REBBAH, AND PH. LABBÉ, *Z. Kristallogr.* **192,** 223 (1990).
12. H. G. VON SCHNERING AND W. HÖNLE, *Chem. Rev.* **88,** 243 (1988).