JOURNAL OF SOLID STATE CHEMISTRY 98, 133–136 (1992)

The Crystal Structure of $Hg_7Sb_4Br_6$

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

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

Received July 30, 1991; in revised form October 28, 1991

The crystal structure of $Hg_7Sb_4Br_6$ (previously reported as HgSbBr) has been solved by the X-ray single crystal technique. $Hg_7Sb_4Br_6$ crystallizes in the cubic system, space group $Pa3$, $Z = 4$, with cell dimensions $a = 12.9940(9)$ Å. The structure consists of the three-dimensional positively charged $[Hg_6Sb_4]^{4+}$ shell, and octahedral $[HgBr_6]^{4-}$ anions. The antimony atoms in the shell are bound into Sb_2^{4-} dumbbells with short Sb–Sb distance of 2.77 Å. The possible migration of Hg^{2+} ions along the fourfold axis is suggested.

Introduction

Cadmium and mercury form many pnictide halides. The common structural feature of these phases is the existence of two types of cluster anions of phosphorus and arsenic. The X_2^{4-} dumbbells (X = P,As) were determined in Cd_2AsCl_2 (*1*), $Cd_4X_2I_3$ (*2, 3*), and $Cd_7P_4Cl_6$ (*4*). The $(X^{1-})_\infty^1$ infinite chains (X = P,As) were determined in Cd_2P_3Z (Z = Cl,Br,I) (*5*) and Cd_2As_3Z (Z = Br,I) (*6, 7*). Several phases containing antimony are also known: HgSbBr (*8*), Hg_2SbBr_2 (*9*), $Hg_3Sb_2I_4$, $Hg_4Sb_2I_3$ (*10*), and $Cd_4Sb_2I_3$ (*11*). In most cases only synthesis and the lattice constants are reported. Recently (*12*) we found Sb_2^{4-} dumbbells in $M_4Sb_2I_3$ (M = Cd,Hg). We assumed that the stoichiometry of HgSbBr reported in (*8*) could indicate possible existence of an $(Sb^{-1})_\infty^1$ chain anion. The stoichiometry of this phase has no analogs among phosphide and arsenide halides of cadmium and mercury. Here we report the crystal structure of the phase with composition $Hg_7Sb_4Br_6$ previously and erroneously reported as HgSbBr (*8*).

Experimental

Mercury bromide ($HgBr_2$), antimony powder, and liquid mercury were mixed in the molar ratio 1 : 2 : 1 as required for the composition HgSbBr. The mixture was annealed at 593 K for 5 days in sealed quartz-glass ampoules. X-ray powder analysis (Enraf–Nonius FR-552 chamber) of the obtained gray powder indicated the presence of three phases: antimony, antimony bromide ($SbBr_3$), and the phase reported as HgSbBr in (*8*). The Guinier spectrum of the mixture annealed for 12 days at the same conditions does not indicate any changes in phase composition. Black crystals (dark brown after grinding) were selected from the mixture. All reflections on the Guinier spectrum of the crystals and the cubic cell dimensions (a = 12.99Å) were in good agreement with those reported for HgSbBr

* To whom correspondence should be addressed.

0022-4596/92 $5.00

TABLE I

DATA COLLECTION AND REFINEMENT PARAMETERS FOR $Hg_7Sb_4Br_6$

Space group	*Pa*3 (No. 205)
a (Å)	12.9940(9)
V (Å^3)	2194.0(5)
Z	4
ρ_{calc} (g/cm^3)	7.176(1)
μ (cm^{-1})	661.94
λ (Mo$K\alpha$, Å)	0.71069
Temperature of measurement	293 K
Scan mode	$\omega - 2\theta$
sin θ/λ_{max}	0.594
No. of unique reflections	651
No. of reflections used with $F_0 > 4\sigma(F_0)$	345
No. of refined parameters	31
Weights	$1/w = \sigma(F)^2 + 0.005F^2$
R	0.073
R_w	0.073

(*8*). These facts enable us to suggest another composition for this phase. The composition $Hg_7Sb_4Br_6$ was determined from the structure determination.

A black crystal of almost cubic form (with approximate dimensions of 0.3 mm) was selected for structure determination and mounted on a Enraf–Nonius CAD4 diffractometer. The unit cell dimensions were determined on the basis of 24 well-centered reflections in the angular range of $16° < \theta < 19°$ and were in good agreement with powder diffraction data. The systematic absences are uniquely consistent with the space group *Pa*3 (No. 205). The data collection parameters are listed in Table I. A semiempirical absorption correction was applied based on ψ-scans of four reflections. The intensities were corrected for Lorentz and polarization effects.

Five atoms (Hg1, Hg2, Sb1, Sb2, and Br1) were located by direct methods. Atomic coordinates and their anisotropic thermal parameters were refined to $R = 0.093$ and $R_w = 0.097$. The $\rho(x, y, z)$ and $\Delta\rho(x, y, z)$ synthesis computed after the refinement of atomic parameters showed the additional peak of electron density of 9.5 e/Å^3 heights at the special position 4*b* (*13*), which was 3.32 Å from the Sb1 atom. This peak was introduced in the refinement as Hg with the appropriate occupancy. The occupancies of 4*a* and 4*b* positions were then included in the refinement, which has led to $R = 0.073$ and $R_w = 0.73$ and to the atomic parameters listed in Table II. The occupancies of the remaining atoms did not change after including them in the refinement. The $\rho(x, y, z)$ and $\Delta\rho(x, y, z)$ synthesis computed after the refinement showed that the remaining peaks were less than 4.4 e/Å (the highest one was 0.61 Å from the Sb1 atom). All data analyses were carried out using CSD programs (*14*).

Description of the Structure and Discussion

The crystal structure of $Hg_7Sb_4Br_6$ is schematically drawn on Fig. 1. All antimony atoms and part of the mercury atoms (Hg1) form a shell with holes of two types. The bigger holes with the center at special position 4*a* (*13*) are filled with the [$HgBr_6$] octahedra, while the smaller ones with the center at special position 4*b* (*13*) are filled with mercury atoms (Hg3).

The antimony atoms possess the tetrahe-

TABLE II

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	x/a	y/b	z/c	$B_{iso/eq}$
Hg1	0.5468(2)	0.3141(2)	0.3033(2)	2.32(8)
Hg2[a]	0	0	0	1.5(2)
Sb1	0.3526(3)	—	—	0.70(7)
Sb2	0.2296(2)	—	—	0.55(6)
Br1	0.4545(5)	0.0509(5)	0.2942(5)	1.6(2)
Hg3[b]	0	0	½	3.6(4)

[a] Occupancy = 0.70(3).
[b] Occupancy = 0.30(3).

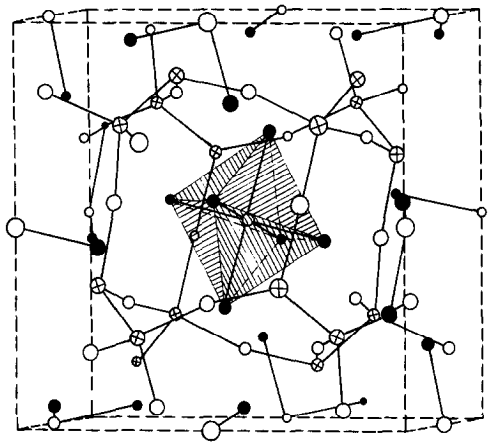

FIG. 1. The crystal structure of $Hg_7Sb_4Br_6$. The origin is at the center of the cube. Open circles, mercury; crossed circles, antimony; closed circles, bromine. The $[HgBr_6]$ octahedron is indicated with hatching at center.

dral coordination of three mercury atoms and one antimony atom with a short Sb–Sb distance of 2.77 Å (Table III), which is close to that in $M_4Sb_2I_3$ (M = Cd, Hg) (*12*). The coordination of the mercury atoms (Hg1) in the shell somewhat deviates from linear with an Sb–Hg–Sb angle of 166.1°. This coordination is usual for mercury in the formal oxidation state of +2 (*15*).

TABLE III

INTERATOMIC BOND DISTANCES (Å), ANGLES (°), AND IMPORTANT NONBONDING DISTANCES (Å)

Distances	Angles
Hg1–Sb1 2.652(5)	Sb1–Hg1–Sb2 165.9(2)
–Sb2 2.651(4)	
Hg2—Br1 2.818(7) (6×)	Br1–Hg2–Br1 91.5(2) (6×)
	Br1–Hg2–Br1 180.0(2) (3×)
	Br1–Hg2–Br1 88.5(2) (6×)
Sb1–Hg1 2.652(5) (3×)	Hg1–Sb1–Hg1 111.4(2) (3×)
–Sb2 2.768(5)	Hg1–Sb1–Sb2 107.5(2) (3×)
Sb2–Hg1 2.651(4) (3×)	Hg1–Sb2–Hg1 107.05(14) (3×)
–Sb1 2.768(5)	Hg1–Sb2–Sb1 111.8(2) (3×)
Br1–Hg2 2.818(7)	
Important nonbonding distances	
Hg1–Br1 3.325(9)	Hg3–Sb1 3.317(4) (2×)
–Br1 3.364(9)	
–Br1 3.445(9)	

The Hg2 atoms are located at the center of an almost regular octahedron of bromine atoms (Table III). The bromine atoms are connected to only one Hg2 atom. The distance between bromine atoms and Hg1 atoms from the shell is longer than 3.32 Å and can not be considered a bonding distance. Such an isolated octahedron $[HgBr_6]$ (but considerably distorted) was found in Tl_4HgBr_6 (*16*).

The crystal structure of $Hg_7Sb_4Br_6$ is closely related to that of $Cd_7P_4Cl_6$ (*4*). However, numerous differences need to be pointed out. The chlorine atoms in $Cd_7P_4Cl_6$ are additionally bound to one cadmium atom from the shell (d_{Cd-Cl} = 2.76 Å, compared with d_{Cd-Cl} = 2.66 Å in the $[CdCl_6]$ octahedron), while bromine atoms in $Hg_7Sb_4Br_6$ are terminal (Table III), and consequently, the $[HgBr_6]$ octahedra are isolated. The 4*b* site filled with mercury atoms with the occupancy of 0.3 in $Hg_7Sb_4Br_6$ is empty in the case of $Cd_7P_4Cl_6$. However, the relatively high R-factor (0.098) for the single crystal structure solution of $Cd_7P_4Cl_6$ (*4*) provides the uncertainty in some details of this structure, especially whether the Cd2 atom is split like Hg2 atom in the structure of $Hg_7Sb_4Br_6$.

The interesting feature of the structure of $Hg_7Sb_4Br_6$ is the alternation of holes of two different sizes along the three fourfold axes. The Hg3 atoms located at the center of the smaller holes have the nearest neighbors (Sb1) at the distance of 3.32 Å, which is too large to be considered the bonding distance. This fact together with the partial occupancy of 4*a* and 4*b* positions by mercury atoms (Table II) could possibly indicate the migration of mercury atoms along the three fourfold axes. In this case we assume that the idealized structure of $Hg_7Sb_4Br_6$ consists of the infinite three-dimensional positively charged shell $(Hg_6Sb_4)^{4+}$ and the isolated octahedral anions $(HgBr_6)^{4-}$, while the 4*b* sites are empty (Fig. 2). It would seem that octahedral

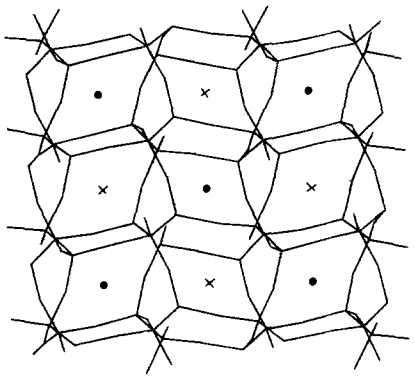

FIG. 2. A view of the idealized crystal structure of $Hg_7Sb_4Br_6$ along the (010) direction. The two-dimensional sequences of filled and vacant holes in the (x ½ z) plane are shown. [$HgBr_6$] octahedra are omitted. Centers of filled holes are marked with crosses; centers of vacant holes are marked with closed circles.

anions of another composition but with the same charge and dimensions could be substituted for $(HgBr_6)^{4-}$ anions without destroying the charged $(Hg_6Sb_4)^{4+}$ shell.

References

1. A. REBBAH, J. YAZBECK, A. LECLAIRE, AND A. DESCHANVRES, *Acta Crystallogr. Sect. B* **36,** 771 (1980).
2. J. GALLAY, G. ALLAIS, AND A. DESCHANVRES, *Acta Crystallogr. Sect. B* **31,** 2274 (1975).
3. A. REBBAH, J. YAZBECK, AND A. DESCHANVRES, *Acta Crystallogr. Sect. B* **36,** 1747 (1980).
4. A. REBBAH, J. YAZBECK, AND A. DESCHANVRES, *Rev. Chim. Miner.* **17,** 96 (1980).
5. P. C. DONOHUE, *J. Solid State Chem.* **5,** 71 (1972).
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* **44,** 77 (1988).
8. H. PUFF AND H. GOTTA, *Z. Anorg. Allg. Chem.* **337,** 157 (1965).
9. H. PUFF AND H. GOTTA, *Z. Anorg. Allg. Chem.* **343,** 225 (1966).
10. H. PUFF AND H. GOTTA, *Z. Anorg. Allg. Chem.* **333,** 280 (1964).
11. H. PUFF AND H. GOTTA, *Z. Anorg. Allg. Chem.* **341,** 324 (1965).
12. A. V. SHEVELKOV, E. V. DIKAREV, AND B. A. POPOVKIN, *J. Solid State Chem.* **93,** in press (1991).
13. "International Tables for X-Ray Crystallography," Vol. 1, p. 314, Kynoch Press, Birmingham(1968).
14. L. G. AKSELRUD, YU. N. GRYN, P. YU. ZAVALIY, V. K. PECHARSKY, AND V. S. FUNDAMENSKY, "Report on the 12th European Crystallographic Meeting, Moscow," p. 155 (1989).
15. A. F. WELLS, "Structural Inorganic Chemistry," 5th ed., Clarendon Press, Oxford (1986).
16. K. BRODERSEN, G. THIELE, AND G. GOERZ, *Z. Anorg. Allg. Chem.* **401,** 217 (1973).