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The Crystal Structures of $Hg_4Sb_2I_3$ and $Cd_4Sb_2I_3$

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The crystal structures of $Hg_4Sb_2I_3$ and $Cd_4Sb_2I_3$ have been solved by X-ray single crystal techniques. $Hg_4Sb_2I_3$ and $Cd_4Sb_2I_3$ are isostructural and crystallize in the cubic system, space group $Pa3$, $Z = 8$, with cell dimensions $a = 13.4392(6)$ Å for $Hg_4Sb_2I_3$ and $a = 13.4876(5)$ Å for $Cd_4Sb_2I_3$. The compounds have a three-dimensional array built from six-membered rings containing mercury (cadmium), antimony, and iodine atoms. One-half of the antimony atoms are bound into Sb_2^{4-} pairs with an Sb–Sb distance of 2.75 Å. The absence of Hg–Hg (or Cd–Cd) and Sb–I bonding was determined. © 1991 Academic Press, Inc.

Introduction

We are investigating clusters of bismuth, mercury, and antimony in binary and complex halides (*1*). The stoichiometry of the compounds $Hg_4Sb_2I_3$ and $Cd_4Sb_2I_3$ reported in (*2, 3*) can not be described in terms of ordinary mercury cations and iodine and antimony anions. The compound with the same stoichiometry $Cd_4P_2I_3$ (*4*) contains P_2^{4-} dumbbells. However, the compounds $Cd_4P_2I_3$ and $Cd_4Sb_2I_3$ are not isostructural since their X-ray diffractograms are quite different. These facts enable us to suggest that $Hg_4Sb_2I_3$ and $Cd_4Sb_2I_3$ should contain clusters of mercury (cadmium) or antimony. We report here on the structure of the $Hg_4Sb_2I_3$ and $Cd_4Sb_2I_3$.

Experimental

$Hg_4Sb_2I_3$ (**I**) and $Cd_4Sb_2I_3$ (**II**) were synthesized from the stoichiometric mixtures of Hg, HgI_2, and Sb (**I**) and Cd, CdI_2, and Sb (**II**) by annealing them in sealed quartz-glass ampoules at 623 K (**I**) and 703 K (**II**) for 5 days. Black (**I**) and dark-red (**II**) powders were obtained. X-ray powder analysis (Enraf-Nonius FR-552 chamber) did not indicate any traces of source materials. All lines on Guinier spectra were in good agreement with those reported in (*2, 3*)

Black (**I**) and dark-red (**II**) single crystals of almost spherical form (0.03 mm in diameter) were selected for structure determination and mounted on a Enraf-Nonius CAD4 diffractometer. The unit cell dimensions were determined on the basis of 25 well-centered reflections in the angular range $17° < \Theta < 20°$. The systematic absences are uniquely consistent with the space group $Pa3$ (No. 205). The data were collected at 293 K with data collection parameters listed in Table I. A semiempirical absorption correction was applied based on the ψ-scans of four reflections. The intensities were corrected for Lorentz and polarization effects. In both cases all atoms were located by the

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TABLE I

DATA COLLECTION AND REFINEMENT PARAMETERS

Phase	$Hg_4Sb_2I_3$	$Cd_4Sb_2I_3$
Space group	$Pa\bar{3}$ (No. 205)	
a (Å)	13.4392(6)	13.4876(5)
V (Å^3)	2427.3(3)	2453.6(3)
Z	8	8
$\rho_{calc.}$ (g/cm^3)	7.810(1)	5.813(1)
μ (cm^{-1})	635.13	187.03
λ (Mo$K\alpha$)	0.71069 Å	
Temperature of measurement	293 K	
Scan mode	$\omega - 2\Theta$	$\omega - 2\Theta$
Sin Θ/λ_{max}	0.616	0.701
Total No. of reflections	891	1308
No. of reflections used with $F_o > 6\sigma(F_o)$	428	704
No. of refined parameters	28	28
Weights	$w = 1$	$w = 1$
R	0.065	0.054
R_w	0.065	0.054

direct methods. Atomic coordinates and their anisotropic thermal parameters were refined with unit weights to $R = 0.065$, $R_w = 0.065$ (**I**) and $R = 0.054$ (**II**) and to the atomic parameters listed in Table II. All data analysis was carried out using CSD programs (*5*).

Description of the Structure and Discussion

The most interesting feature of these compounds is the existence of short Hg–Sb (Cd–Sb) and Sb–Sb distances and the absence of short Sb–I and Hg–Hg (Cd–Cd) contacts (Tables III and IV).

All atoms in both structures are joined into nonplanar six-membered rings (Fig. 1). Each ring contains three mercury (cadmium), two antimony, and one iodine atom. The two principle types of ring sharing are drawn schematically in Fig. 2. In the first case (Fig. 2a) three rings are stacked via a common Sb2 atom which is additionally linked along the [111] direction to the Sb2 atom from the neighboring triplet of rings with the Sb–Sb distance of 2.75 Å, which is shorter than the Sb–Sb distance in metal (*6*) (d_{Sb-Sb} = 2.91 Å). In the second case (Fig. 2b) three rings are stacked via a common Hg2–Sb1 (Cd2–Sb1) bond. The two types of ring sharing provide a three-dimensional system of six-membered rings, involving every mercury (cadmium), antimony, and iodine atom. Antimony atoms in $Hg_4Sb_2I_3$ are located in the centers of the almost regular tetrahedra of the two types. The Sb1 atoms are surrounded by four mercury atoms and the Sb2 atoms are surrounded by three mercury atoms and one antimony atom with Hg–Sb distances ranging from 2.66 to 2.69 Å (Table III). The Hg1 atom possesses the planar triangle coordination of two antimony atoms and one iodine atom with the additional iodine atom at a considerably long Hg1–I distance, 3.44 Å. The Hg2 atoms are located in the centers of distorted tetrahedra built from one antimony atom and three iodine atoms. All atoms in $Cd_4Sb_2I_3$ show the same coordination.

It is interesting that the cell dimensions of the isostructural compounds $Hg_4Sb_2I_3$ and $Cd_4Sb_2I_3$ are nearly the same (Table I). More than that, the Hg–I and Cd–I distances ranging from 2.96 to 3.03 Å (Tables III and IV)

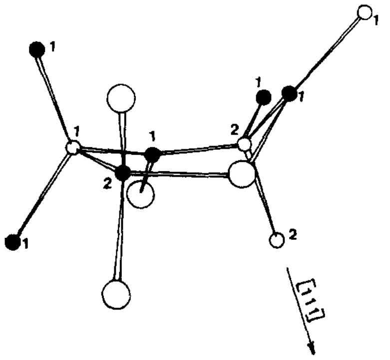

FIG. 1. The main fragment of the $M_4Sb_2I_3$ (M = Hg, Cd) structures. Six-membered rings. For each atom involved in the ring the nearest neighbors are also shown. Black circles, mercury (cadmium); small open circles, antimony; large open circles, iodine.

TABLE II

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	x/a	y/b	z/c	$B_{iso/eq}$
		1. $Hg_4Sb_2I_3$		
Hg1	0.0270(2)	0.0032(2)	0.2471(2)	2.52(6)
Hg2	0.7849(2)	$1 - x$	$\frac{1}{2} - x$	4.13(7)
Sb1	0.9003(2)	$1 - x$	$\frac{1}{2} - x$	0.48(5)
Sb2	0.5591(3)	$x - \frac{1}{2}$	$1 - x$	0.78(5)
I1	0.2474(3)	0.1889(2)	0.5669(2)	0.87(7)
		2. $Cd_4Sb_2I_3$		
Cd1	0.0261(1)	0.0144(2)	0.2530(1)	2.85(4)
Cd2	0.7817(1)	$1 - x$	$\frac{1}{2} - x$	2.87(3)
Sb1	0.8991(1)	$1 - x$	$\frac{1}{2} - x$	1.22(2)
Sb2	0.5588(1)	$x - \frac{1}{2}$	$1 - x$	1.23(2)
I1	0.2437(1)	0.1868(1)	0.5680(1)	1.67(3)

are much larger than in corresponding binary iodides (*7*). It is evident that the analogous compound with zinc instead of mercury or cadmium can not exist since the Zn–I distances should be larger in this case than the appropriate Zn–I bonding distance.

The fairly short contact Sb2–Sb2 (2.75 Å) indicates possibly the existence of an Sb_2^{4-} complex. The cluster of the same type P_2^{4-} with the same coordination of phosphorus has been described in $Cd_4P_2I_3$ (*4*). In this case it should be proposed that the Sb2 atom

TABLE III

INTERATOMIC BOND DISTANCES (Å), ANGLES (°) AND MAIN NONBONDING DISTANCES (Å) FOR $Hg_4Sb_2I_3$

Distances		Angles	
Hg1—Sb1	2.665(4)	Sb1—Hg1—Sb2	144.8(2)
—Sb2	2.672(4)	Sb1—Hg1—I1	118.66(13)
—I1	3.026(4)	Sb2—Hg1—I1	95.65(13)
Hg2—Sb1	2.686(4)	Sb1—Hg2—I1	126.47(14) (3×)
—I1	2.994(4) (3×)	I1—Hg2—I1	88.28(12) (3×)
Sb1—Hg1	2.665(4) (3×)	Hg1—Sb1—Hg1	119.57(14) (3×)
—Hg2	2.686(4)	Hg1—Sb1—Hg2	93.76(13) (3×)
Sb2—Hg1	2.672(4) (3×)	Hg1—Sb2—Hg1	111.9(2) (3×)
—Sb2	2.751(5)	Hg1—Sb2—Sb2	106.9(2) (3×)
I1—Hg2	2.994(4)	Hg1—I1—Hg2	112.66(13)
—Hg1	3.026(4)		
		Main nonbonding distances	
Hg1—I1	3.434(5)	Hg2—Hg1	3.906(4) (3×)
—I1	3.745(4)	—I1	4.034(4) (3×)
—Hg2	3.906(4)	Sb1—I1	4.159(5) (3×)
—I1	3.913(4)	Sb2—I1	4.229(5) (6×)

TABLE IV

INTERATOMIC BOND DISTANCES (Å), ANGLES (°), AND MAIN NONBONDING DISTANCES (Å) FOR $Cd_4Sb_2I_3$

Distances		Angles	
Cd1—Sb1	2.705(2)	Sb1—Cd1—Sb2	140.07(9)
—Sb2	2.723(2)	Sb1—Cd1—I1	119.38(8)
—I1	2.961(2)	Sb2—Cd1—I1	96.78(7)
Cd2—Sb1	2.744(2)	Sb1—Cd2—I1	125.43(8) (3×)
—I1	2.958(2) (3×)	I1—Cd2—I1	89.77(6) (3×)
Sb1—Cd1	2.705(2) (3×)	Cd1—Sb1—Cd1	118.43(8) (3×)
—Cd2	2.744(2)	Cd1—Sb1—Cd2	97.26(7) (3×)
Sb2—Cd1	2.723(2) (3×)	Cd1—Sb2—Cd1	109.57(7) (3×)
—Sb2	2.747(2)	Cd1—Sb2—Sb2	109.38(7) (3×)
I1—Cd2	2.958(2)	Cd1—I1—Cd2	111.98(7)
—Cd1	2.961(2)		

Main nonbonding distances

Cd1—I1	3.247(2)	Cd2—Cd1	4.089(3) (3×)
—I1	3.941(2)	—I1	4.100(2) (3×)
—I1	3.967(3)	Sb1—I1	4.217(2) (3×)
—Cd2	4.089(3)	Sb2—I1	4.243(2) (3×)
		—I1	4.253(2) (3×)

(electron configuration $5s^25p^5$) gives one electron to form a homonuclear Sb–Sb bond, while three lone pairs interact with vacant orbitals of three mercury atoms. Then, four lone pairs of the Sb1 atom (electron configuration $5s^25p^6$ for oxidation state −3) interact with vacant orbitals of four mercury atoms. Planar triangle and tetrahedral coordinations of mercury atoms are usual for mercury in oxidation state +2 (*7*, *8*). Assuming the iodine atom to be in oxidation state −1 we can suggest the following crystallochemical formulas: $(M^{2+})_4(Sb_2^{4-})_{1/2}(Sb^{3-})_1(I^{1-})_3$, where M = Cd, Hg.

One can expect indeed that the arrangement of Sb–Sb pairs along the [111] direc-

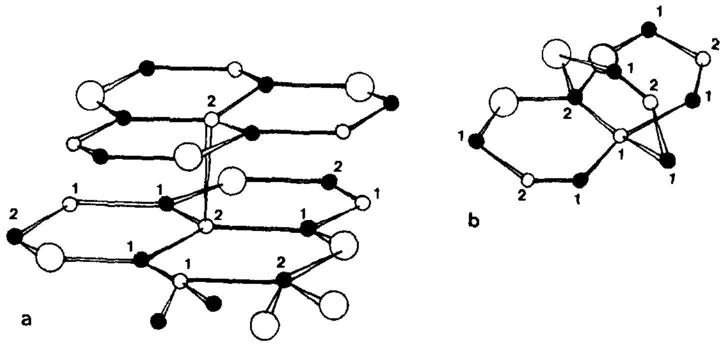

FIG. 2. Two types of ring linkage. Rings are drawn as planar for the sake of simplicity. Black circles, mercury (cadmium); small open circles, antimony; large open circles, iodine.

tion should cause the anisotropy of physical (in particular electrophysical) properties along this direction.

We have also determined the existence of Sb_2^{4-} dumbbells in the compound previously reported as $Hg_3Sb_2I_4$ (*2*). A single crystal structure solution enables us to suppose another stoichiometry. Structure refinement is in progress and will be a topic of a separate article.

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