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The Syntheses of Hg_2P_3X Where X = Cl and Br

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Two new mercury halophosphides Hg_2P_3Cl and Hg_2P_3Br, have been prepared. Hg_2P_3Cl has the monoclinic Cd_2P_3Cl structure $a = 7.840$ Å, $b = 8.849$ Å, $c = 7.593$ Å, $\beta = 98.63°$. Hg_2P_3Br has a related orthorhombic structure $a = 8.014$ Å, $b = 8.901$ Å, $c = 7.822$ Å. Both are black semiconductors stable in HCl and HNO_3.

Introduction

Mercury forms many pnictide halides; $Hg_4As_2X_3$ (X = Cl, Br, I), Hg_2AsCl_2, Hg_3PCl_2, Hg_2SbBr_2 (*1*), HgAsCl, Hg_2AsBr_2, $Hg_3As_2I_4$ (*2*), HgSbBr, $Hg_4Sb_2I_3$, Hg_3SbI_4 (*3, 4*), Hg_2SbBr_5, $HgSbBr_5$ (*5*), Hg_2SbCl_5, $HgSbCl_5$ (*6*), Hg_3PCl_3, $Hg_5P_2Br_4$ (*7*), Hg_2PCl_2, Hg_2PBr_2, $Hg_3P_2Cl_2$, $Hg_4As_2Cl_3$ (*8*). In most cases, only syntheses, stoichiometry, and lattice constants are reported; little is known of the structures or electrical properties. Most are either black or colored, suggesting they are semiconductors. This paper reports an extension of the halopnictide series to include the compounds Hg_2P_3X where X = Cl and Br, the first examples in which the pnictide is in excess of the halide.

Experimental

Hg_2P_3Cl and Hg_2P_3Br were prepared by reaction of $HgCl_2$ or $HgBr_2$ with Hg and P weighed in stoichiometric proportions and sealed *in vacuo* in silica tubes ($\frac{5}{8}$ in. o.d. × $\frac{3}{8}$ in. i.d. × 6 in.). All syntheses were carried out in a pressure vessel with 150–200 atm nitrogen surrounding the silica reaction tube to prevent explosion due to high vapor pressures developed during reactions. Typical conditions were: sample held at 500°C for 10 hr, slowly cooled 20 hr to 300°C, and then rapidly cooled to room temperature by turning off furnace power. For the preparation of Hg_2P_3Cl, a charge of about 20 g was effective while 1 or 2 g charges in tubes of the same volume failed to yield the phase. This suggests that some internally developed pressure is necessary to stabilize the compound. Traces of other phases, including PCl_3 and Hg, were present; these were removed by washing in concentrated HNO_3. Nearly 100% yields were obtained for Hg_2P_3Br. Solid solutions were prepared in a similar manner. Powder X-ray diffraction was carried out on all samples using a Hägg–Guinier camera with Cu$K\alpha$, radiation and an internal standard of high-purity KCl ($a = 6.29310$ Å at 25°C). The lattice constants were refined by a least-squares technique. Single-crystal determinations of space groups utilized Buerger precession camera techniques. Electrical measurements were made using a four-probe technique between 300 and 4.2 K. A Du Pont differential scanning calorimeter and a Du Pont 700 thermal analyzer were used for thermal analyses.

Results and Discussion

Hg_2P_3Cl

The chlorophosphide forms as black shiny crystals insoluble in strong acids.

Anal. Calcd Cl, 6.69%; P, 17.54%. Found Cl, 6.69 ± 0.2%; P, 17.11 ± 0.3%. It has monoclinic space group $C2/c$ with $a = 7.840(1)$ Å, $b = 8.849(1)$ Å, $c = 7.593(1)$ Å, $\beta = 98.63°$. The Guinier pattern is shown in Table I. Decomposition in argon begins at about 400°C.

* Contribution no. 1915.

TABLE I

GUINIER X-RAY POWDER DIFFRACTION PATTERNS

Hg_2P_3Br				Hg_2P_3Cl			
I	$h\,k\,l$	d(obsd)	d(calcd)	I	$h\,k\,l$	d(obsd)	d(calcd)
20	1 1 0	5.9493	5.9556	40	−1 1 1	4.8805	4.8780
10	1 1 1	4.7344	4.7384	75	1 1 1	4.3728	4.3711
70	0 2 0	4.4488	4.4504	75	2 0 0	3.8752	3.8746
80	2 0 0	4.0056	4.0069	90	0 2 1	3.8123	3.8107
45	0 2 1	3.8663	3.8681	75	0 0 2	3.7547	3.7528
95	1 0 2	3.5151	3.5147	60	−1 1 2	3.3313	3.3311
95	1 2 1	3.4839	3.4836	85	1 1 2	3.0055	3.0049
70	2 1 1	3.3096	3.3104	50	−2 0 2	2.9238	2.9236
40	1 1 2	3.2681	3.2691		2 2 0		2.9145
75	2 2 0	2.9773	2.9778	30	0 2 2	2.8618	2.8616
80	2 0 2	2.7981	2.7988	100	−2 2 1	2.8276	2.8266
100	2 2 1	2.7833	2.7830	10	1 3 0	2.7566	2.7560
	1 3 0		2.7824	15	−1 3 1	2.6320	2.6330
95	1 2 2	2.7584	2.7583	65	2 2 1	2.6193	2.6190
65	2 1 2	2.6698	2.6699	10	1 3 1	2.5444	2.5436
25	1 3 1	2.6213	2.6215	5	2 0 2	2.5145	2.5138
60	3 1 1	2.4314	2.4318	10	3 1 0	2.4791	2.4795
35	1 1 3	2.3882	2.3884	75	−1 1 3	2.3996	2.3992
15	2 2 2	2.3691	2.3692	60	−1 3 2	2.2807	2.2801
95	0 2 3	2.2497	2.2497	40	3 1 1	2.2598	2.2595
90	3 0 2	2.2060	2.2058	80	0 4 0	2.2113	2.2116
75	3 2 1	2.1982	2.1981		1 1 3		2.2105
60	1 2 3	2.1659	2.1659	45	1 3 2	2.1675	2.1669
60	0 4 1	2.1405	2.1403	5	0 4 1	2.1222	2.1214
	3 1 2		2.1411	25	−2 2 3	2.0143	2.0140
15	2 1 3	2.1224	2.1223	45	3 1 2	1.9436	1.9440
75	1 4 1	2.0679	2.0678		3 3 0		1.9430
25	2 3 2	2.0359	2.0359	20	4 0 0	1.9377	1.9373
40	4 0 0	2.0034	2.0035		−3 3 1		1.9347
50	3 3 0	1.9852	1.9852	50	2 4 0	1.9210	1.9207
35	3 2 2	1.9766	1.9764	75	−1 3 3	1.9043	1.9037
45	2 2 3	1.9616	1.9616		−3 1 3		1.9034
35	0 0 4	1 9558	1 9555		0 4 2		1.9053
5	2 4 0	1.9454	1.9454	40	−1 1 4	1.8479	1.8480
5	0 4 2	1.9340	1.9341	30	3 3 1	1.8316	1.8315
10	3 3 1	1.9242	1.9242		2 4 1		1.8284
20	1 3 3	1.9019	1.9025	20	−3 3 2	1.8112	1.8109
	1 0 4		1.8997	15	1 3 3	1.8054	1.8051
55	4 1 1	1.8964	1.8963	40	−4 2 1	1.7827	1.7826
60	2 4 1	1.8878	1.8879	10	4 2 0	1.7747	1.7745
50	1 4 2	1.8802	1.8801	35	−2 4 2	1.7646	1.7638
60	4 2 0	1.8267	1.8269	10	1 1 4	1.7302	1.7301
	3 1 3		1.8261		0 2 4		1.7274
20	0 2 4	1.7904	1.7903	15	−1 5 1	1.6937	1.6935
10	4 0 2	1.7832	1.7831		−4 2 2		1.6968
15	3 3 2	1.7704	1.7702	10	4 2 1	1.6764	1.6761
75	2 0 4	1.7577	1.7574	15	1 5 1	1.6688	1.6690
	2 3 3		1.7596		−2 2 4		1.6655
40	4 1 2	1.7480	1.7484	20	3 3 2	1.6509	1.6511
	1 2 4		1.7472	15	3 1 3	1.6467	1.6466
20	2 4 2	1.7420	1.7418	10	−3 3 3	1.6256	1.6260
10	1 5 0	1.7381	1.7378		4 0 2		1.6250
15	2 1 4	1.7241	1.7241	35	−3 1 4	1.6121	1.6121
				20	2 0 4	1.5973	1.5974
				35	−1 3 4	1.5911	1.5910
				10	−2 4 3	1.5813	1.5814

Hg_2P_3Cl is a semiconductor ($\rho_{298K} = 6.89 \times 10^8$ Ω-cm) with a small degree of photoconductivity. The cell dimensions are similar to those of Cd_2P_3Cl (*9*); however, the volume is smaller, 520.8 Å^3 compared to 532.6 Å^3 for Cd_2P_3Cl.

Hg_2P_3Br

The bromophosphide also occurs as black shiny crystals insoluble in strong acid. *Anal.* Calcd Hg, 69.89%; P, 16.19%; Br, 13.92%. Found Hg, 70.10 ± 0.5%; P, 16.8 ± 0.3%; Br, 13.47 ± 0.3%. Calcd $4(Hg_2P_3Br)$/cell = 6.832 g/cm^3. Density obsd = 6.81 ± 0.02 g/cm^3. This compound is orthorhombic with space group *Pbcn*. Cell dimensions are $a = 8.014(1)$ Å, $b = 8.901(1)$ Å, $c = 7.822(1)$ Å. The powder pattern is shown in Table I. Hg_2P_3Br is a semiconductor; $\rho_{298K} = 6.0 \times 10^7$ Ω-cm.

The structure of the bromophosphide may be related to the Cd_2P_3Cl type by an adjustment of β to 90°. A structure determination would be of interest to compare the structures.

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